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MATHEMATIK

ZUR LAPLACE-TRANSFORMATION. V

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Wir gehen aus von dem Laplace Integral

$$f(z) = \int_a^\infty e^{-zt} F(t)\, dt, \tag{1}$$

wobei a reell und endlich angenommen ist.

Im Falle absoluter Konvergenz des Integrals (1) gilt bekanntlich die Umkehrformel

$$F(t) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{zt} f(z)\, dz; \tag{2}$$

d. h. führen wir in (2) das aus (1) auf Grund eines gegebenen $F(t)$ bestimmte $f(z)$ ein, so kommen wir, bei absoluter Konvergenz des Integrals (1), wieder zu unserer Ausgangsfunktion $F(t)$ zurück.

Hierbei ist $f(z)$ eine reguläre analytische Funktion der komplexen Veränderlichen $z=x+iy$, in der ganzen Halbebene, rechts von der Geraden $x = c$.

Ist umgekehrt $f(z)$ gegeben und führen wir die jetzt aus (2) bestimmte Funktion $F(t)$ in (1) ein, so erhalten wir, im allgemeinen, unsere Ausgangsfunktion $f(z)$, und (1) ist absolut konvergent, falls das Integral

$$\int_{-\infty}^{+\infty} |f(c+iy)|\, dy \tag{3}$$

existieren wird *.

Da nun gerade dieser Übergang von $f(z)$ zu $F(t)$ für die Anwendungen von besonderer Wichtigkeit ist, scheint es von Interesse zu sein solche Bedingungen für $f(z)$ anzugeben, bei welchen dieser Übergang immer möglich sein wird und zugleich das Integral (1) absolut konvergiert. Letzteres ermöglicht uns auch, wie eingangs bemerkt, wieder mittelst (2) zu $F(t)$ zu kommen.

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* Diese vorliegende Note kann in gewissem Sinne als Ergänzung zu einem Ergebnis der Arbeit von Haar (1), S. 73—76, betrachtet werden.

Eine solche vollkommene Reziprozität zwischen $f(z)$ und $F(t)$ wird nun immer bestehen, falls sich $f(z)$ in der oben erwähnten Halbebene für grosse $|z|$ darstellen lässt in der Form:

$$f(z) = \frac{A + B \log z}{z^{\nu}} e^{-az}, \tag{4}$$

mit

$$\nu > 0, \tag{5}$$

wobei A und B Konstanten bedeuten. Es wird dann

$$F(t) = 0; \quad t < a \tag{6}$$

sein, wobei rechts in (6) $t \leqslant a$ stehen muss, falls

$$\nu > 1 \tag{7}$$

sein wird.

Vorerst müssen wir die absolute Konvergenz des Integrals (1) nachweisen. Aus (2) erhalten wir:

$$F(t) = \frac{e^{ct}}{2\pi} \int_{-\omega}^{+\omega} e^{iyt} f(c + iy)\, dy +$$

$$+ \frac{e^{ct}}{2\pi} \left\{ \int_{\omega}^{\infty} e^{iyt} f(c + iy)\, dy + \int_{\omega}^{\infty} e^{-iyt} f(c - iy)\, dy \right\}. \tag{8}$$

Wir bezeichnen:

$$g(t) = (t - a)\, e^{ct} \int_{\omega}^{\infty} e^{iyt} f(c + iy)\, dy. \tag{9}$$

Dann ergibt sich bei genügend grossen ω wegen (4):

$$g(t) = A(t - a)\, e^{c(t-a)} \int_{\omega}^{\infty} \frac{e^{iy(t-a)}}{(c + iy)^{\nu}}\, dy = \frac{A e^{c(t-a)}}{i} \int_{\omega}^{\infty} \frac{d e^{iy(t-a)}}{(c + iy)^{\nu}}, \tag{10}$$

wo wir einfachheitshalber in (4) $B = 0$ gesetzt haben. Der Fall $B \neq 0$ lässt sich in analoger Weise leicht erledigen. Durch partielle Integration folgt aus (10):

$$|g(t)| = A e^{c(t-a)} \left| \frac{-e^{i\omega(t-a)}}{(c + i\omega)^{\nu}} + i\nu \int_{\omega}^{\infty} \frac{e^{iy(t-a)}}{(c + iy)^{\nu+1}} \right| <$$

$$< A e^{c(t-a)} \left\{ \frac{1}{(\sqrt{c^2 + \omega^2})^{\nu}} + \nu \int_{\omega}^{\infty} \frac{dy}{(\sqrt{c^2 + y^2})^{\nu+1}} \right\} = D e^{c(t-a)}. \tag{11}$$

Es soll nun ω, wenn auch gross, aber fest sein. Es ist dann D in (11) eine Konstante und dasselbe gilt auch für

$$M = \int_{-\omega}^{+\omega} |f(c + iy)|\, dy. \tag{12}$$

Da wir nun in (8) für das zweite Glied in Klammern ein zu (11) analoges Resultat erhalten, so ergibt uns deshalb (8):

$$|(t - a) F(t)| < \frac{M}{2\pi} (t - a)\, e^{ct} + \frac{D}{\pi} e^{c(t-a)}, \tag{13}$$

und hieraus folgt, falls $x > c$ angenommen:

$$\int_a^\infty e^{-xt} |(t-a) F(t)| \, dt < \frac{M}{2\pi} \frac{e^{-a(x-c)}}{(x-c)^2} + \frac{D}{\pi} \frac{e^{-ax}}{(x-c)}. \tag{14}$$

Da aber augenscheinlich

$$\int_b^\infty e^{-xt} |F(t)| \, dt < \int_b^\infty e^{-xt} |(t-a) F(t)| \, dt, \quad (b > a+1) \tag{15}$$

sein wird, so schliessen wir, falls wir die Funktion

$$f_1(z) = \int_a^\infty e^{-zt} F(t) \, dt \tag{16}$$

einführen, mit $Re(z) = x > c$, auf Grund von (14) und (15), dass das Integral (16) absolut konvergent sein wird, und zwar gilt dies immer bei den Bedingungen (4) und (5).

Wäre noch ausserdem $f_1(z) = f(z)$, so würde die vollkommene Reziprozität zwischen $f(z)$ und $F(t)$ erwiesen sein. Dieses tritt nun tatsächlich auch ein im Falle (7), denn dann existiert das Integral (3).

Nun entsprechen aber bei den Anwendungen viele Integrale gerade dem Fall $0 < \nu \leqq 1$; z. B.:

$$\frac{1}{\sqrt{z^2+1}} = \int_0^\infty e^{-zt} J_0(t) \, dt, \tag{17}$$

wo $J_0(t)$ die Besselsche Funktion nullter Ordnung bedeutet. Es wird deshalb wichtig sein die Gleichheit $f_1(z) = f(z)$ gerade hierbei zu beweisen und somit auch die Reziprozität, welche ja auch bei (17) gültig ist.

Da nun bei $0 < \nu \leqq 1$ das Integral (3) nicht existieren wird, müssen wir bei dem Beweis einen Umweg machen.
Aus (16) folgt

$$\chi_1(z) = -\frac{df_1(z)}{dz} - af_1(z) = \int_a^\infty e^{-zt} (t-a) F(t) \, dt. \tag{18}$$

Ferner fliesst aus (2), mittelst partieller Integration und wegen (4) und (5):

$$F(t) = \frac{1}{2\pi i t} \int_{c-i\infty}^{c+i\infty} f(z) \frac{de^{zt}}{dz} \, dz = -\frac{1}{2\pi i t} \int_{c-i\infty}^{c+i\infty} e^{zt} \frac{df(z)}{dz} \, dz. \tag{19}$$

Hieraus und aus (2) erhalten wir dann

$$(t-a) F(t) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{zt} \chi(z) \, dz, \tag{20}$$

mit

$$\chi(z) = -\frac{df(z)}{dz} - af(z). \tag{21}$$

Für $\chi(z)$ ergibt sich nun bei grossem z aus (4) und (5):

$$\chi(z) = \frac{e^{-az}}{z^{\nu+1}} \{\nu A - B + \nu B \log z\}; \quad \nu > 0. \tag{22}$$

Dieses entspricht aber gerade dem Fall (7). Aus (20) erhalten wir demnach sofort:

$$\chi(z) = \int_a^\infty e^{-zt}(t-a)F(t)\,dt. \tag{23}$$

Hieraus und aus (18) folgt auf Grund des Eindeutigkeitssatzes von Lerch, $\chi_1(z) = \chi(z)$, d. h.

$$\frac{d\{f_1(z)-f(z)\}}{dz} + a\{f_1(z)-f(z)\} = 0. \tag{24}$$

Nach dem Integrieren erhalten wir

$$f_1(z)-f(z) = Ce^{-az}. \tag{25}$$

Die Konstante C muss aber gleich Null sein und zwar auf Grund zweier verschiedener Überlegungen. Erstens muss die Differenz zweier Unterfunktionen wieder eine Unterfunktion ergeben. Die rechte Seite von (25) ist aber keine solche Funktion, ausser bei $C = 0$. Ferner strebt, da das Integral (1) absolut konvergiert, das Produkt $f(z)\,e^{az}$ gegen Null, bei $|z| \to \infty$ innerhalb der erwähnten Halbebene.

Hierdurch hätten wir also die vollkommene Reziprozität zwischen $f(z)$ und $F(t)$ bei den Bedingungen (4) und (5) nachgewiesen.

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[1] A. Haar, Mathem. Ann., **96** (1927).

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MATHÉMATIQUES

SUR UNE GÉNÉRALISATION DE LA SÉRIE DE TAYLOR

Par P. KOROVKIN

(Présenté par S. N. Bernstein, de l'Académie, 25. I. 1937)

Considérons la série

$$\sum_{n=0}^{\infty} c_n p_n(z), \tag{1}$$

où $p_n(z)$ sont des polynômes de degré n:

$$p_n(z) = (z - \alpha_1^{(n)}) \ldots (z - \alpha_n^{(n)}). \tag{2}$$

Dans cette note nous allons étudier la convergence de la série (1) en faisant certaines hypothèses sur la loi de la répartition des racines $\alpha_k^{(l)}$ dans le plan de la variable complexe.

I. Supposons en premier lieu que les racines $\alpha_1^{(n)}, \alpha_2^{(n)}, \ldots, \alpha_n^{(n)}$ ont un nombre fini de points d'accumulation $a_1, \ldots, a_k$, c'est-à-dire, pour chaque nombre arbitraire $\varepsilon > 0$ il existe un $N(\varepsilon)$ tel, que pour chaque n le nombre des points $\alpha_1^{(n)}, \ldots, \alpha_n^{(n)}$, situés en dehors des circonférences de centres $a_1, \ldots, a_k$ et de rayons ε, ne dépasse pas $N(\varepsilon)$. Soit $n_i(\varepsilon)$ le nombre des points $\alpha_1^{(n)}, \alpha_2^{(n)}, \ldots, \alpha_n^{(n)}$, qui appartiennent au cercle $|z - a_i| \leqslant \varepsilon$ $(i = 1, 2, \ldots, k)$. Supposons que pour un choix déterminé de ε nous avons les limites:

$$\rho_i = \lim_{n \to \infty} \frac{n_i(\varepsilon)}{n}. \tag{3}$$

Il suit de la condition précédente que dans ce cas ces limites existent pour ε arbitraire et ne dépendent pas de ε. Supposons enfin que les nombres $\alpha_k^{(l)}$ sont bornés en module:

$$|\alpha_k^l| \leqslant M \qquad (k,\ l = 1,\ 2,\ \ldots). \tag{4}$$

Dans ces conditions il est facile de prouver que la série (1) converge en chaque point z, qui satisfait à la condition:

$$|(z - a_1)^{\rho_1} \ldots (z - a_k)^{\rho_k}| < \frac{1}{m}, \tag{5}$$

où

$$m = \overline{\lim_{n \to \infty}} \sqrt[n]{|c_n|}. \tag{6}$$

Fixons $\varepsilon > 0$ et considérons le terme général de la série (1):

$$c_n p_n(z) = c_n(z-\alpha_1^{(n)}) \dots (z-\alpha_n^{(n)}) =$$

$$= c_n(z-\beta_1^{(n)}) \dots (z-\beta_{N_n}^{(n)})(z-\alpha_{11}^{(n)}) \dots (z-\alpha_{1n_1}^{(n)}) \dots (z-\alpha_{k_1}^{(n)}) \dots (z-\alpha_{kn_k}^{(n)}),$$

où $\beta_s^{(n)}$ sont les points qui n'appartiennent pas aux cercles $|z-a_i| \leqslant \varepsilon$ $(i=1, 2, \dots, k)$. Nous avons $N_n \leqslant N(\varepsilon)$ et, en vertu de (4):

$$\sqrt[n]{|c_n p_n(z)|} \leqslant \sqrt[n]{|c_n|}\,(|z|+M)^{\frac{N_n}{n}} \prod_{i=1}^{k} (|z-a_i|+\varepsilon)^{\frac{n_i(\varepsilon)}{n}},$$

et, par conséquent

$$\overline{\lim_{n\to\infty}} \sqrt[n]{|c_n p_n(z)|} \leqslant m \prod_{i=1}^{k} (|z-a_i|+\varepsilon)^{\rho_i},$$

d'où résulte la proposition à démontrer, parce que nous pouvons choisir ε arbitrairement.

On peut démontrer aussi que, si z n'est pas un point d'accumulation de l'ensemble de tous les points $\alpha_k^{(l)}$ et si

$$|(z-a_1)^{\rho_1} \dots (z-a_k)^{\rho_k}| > \frac{1}{m}$$

la série (1) diverge au point z.

II. Supposons maintenant que les racines des polynômes $p_n(z)$ sont réelles et appartiennent à l'intervalle (a, b), qui est ouvert à gauche et fermé à droite.

Soit $n(x)$ le nombre des racines du polynôme $p_n(z)$ qui appartiennent à l'intervalle (a, x) fermé à droite. Nous supposerons que pour chaque x existe la limite

$$\rho(x) = \lim_{n\to\infty} \frac{n(x)}{n}. \tag{7}$$

La fonction $\rho(x)$ est évidemment une fonction non décroissante, $\rho(a)=0$ et $\rho(b)=1$. Nous allons démontrer que dans les hypothèses faites précédemment la série (1) converge pour chaque z, qui satisfait aux conditions:

$$\int_a^b \ln|z-x|\, d\rho(x) < -\ln m, \tag{8}$$

où m est défini par la formule (6).

Soit $a = x_0 < x_1 < \dots < x_m = b$ et supposons que $(x_k - x_{k-1}) < \varepsilon$ $(k=1, \dots, m)$. Soient $\alpha_{ik}^{(n)}$ $(k=1, \dots, m_i)$ les racines du polynôme $p_n(z)$, qui appartiennent à l'intervalle (x_{i-1}, x_i), ouvert à gauche et fermé à droite. Nous avons:

$$c_n p_n(z) = c_n \prod_{i=1}^{m} \Big(\prod_{k=1}^{m_i} (z-\alpha_{ik}^{(n)}) \Big)$$

et, comme précédemment:

$$\overline{\lim_{n\to\infty}} \sqrt[n]{|c_n p_n(z)|} \leqslant m \prod_{i=1}^{m} (|z-\xi_i|+\varepsilon)^{\rho(x_i)-\rho(x_{i-1})},$$

où ξ_i est un point de l'intervalle (x_{i-1}, x_i). Par conséquent,

$$\log \overline{\lim_{n\to\infty}} \sqrt[n]{|c_n p_n(z)|} \leqslant \log m + \sum_{i=1}^{m} \log(|z-\xi_i|+\varepsilon)[\rho(x_i)-\rho(x_{i-1})].$$

En fixant ε dans l'expression $\log(|z-\xi_i|+\varepsilon)$, nous pouvons écrire:

$$\log \lim_{n\to\infty} \sqrt[n]{|c_n p_n(z)|} \leqslant \log m + \int_a^b \log(|z-x|+\varepsilon)\, d\rho(x),$$

d'où il suit que la série (1) converge, si z satisfait aux conditions:

$$\int_a^b \log(|z-x|+\varepsilon)\, d\rho(x) < -\log m.$$

En faisant tendre ε vers zéro, nous voyons que la proposition est démontrée; si z appartient à l'intervalle (a, b), l'intégrale de la formule (8) peut avoir la valeur $-\infty$.

III. On peut faire d'autres hypothèses sur la loi de répartition des racines $\alpha_k^{(l)}$. Supposons, par exemple, que toutes les racines sont bornées en module et que pour chaque rectangle ω dont les côtés sont parallèles aux axes des coordonnées:

$$p \leqslant x < q, \quad p_1 \leqslant y < q_1 \tag{9}$$

la limite

$$\rho(\omega) = \lim_{n\to\infty} \frac{n(\omega)}{n},$$

existe, où $n(\omega)$ est le nombre des racines du polynôme $p_n(z)$, qui appartiennent au rectangle (9). Dans ce cas la condition (8) prend la forme:

$$\int_{\Omega} \ln|z-x|\, \rho(d\omega) < -\ln m,$$

où Ω est le rectangle, qui contient toutes les racines $\alpha_k^{(l)}$ et l'intégrale est une intégrale de Riemann-Stiltjes.

Pour les cas II et III on peut démontrer, comme pour le cas I, des théorèmes sur la divergence.

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THEORY OF ELASTICITY

CONCERNING A PROBLEM OF THE THEORY OF SHELLS

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(Communicated by A. N. Krylov, Member of the Academy, 5. II. 1937)

As is known, the design of symmetrically loaded shells of revolution has been reduced by Meissner (1) to the integration of two linear differential equations of the fourth order of the type *:

$$LL(\Theta) - \sigma h L\left(\frac{1}{R_1}\Theta\right) + \frac{\sigma h}{R_1} L(\Theta) + \left[-\frac{\sigma^2 h^2}{R_1^2} + \lambda^2\right]\Theta = 0, \qquad (1)$$

$$LL(U) + \sigma h L\left(\frac{1}{R_1}U\right) - \frac{\sigma h}{R_1} L(U) + \left[-\frac{\sigma^2 h^2}{R_1^2} + \lambda^2\right] U = 0, \qquad (2)$$

where $L(\ldots)$ denotes the linear differential operator:

$$L(\ldots) = \frac{R_2 h}{R_1^2}\left[\frac{d^2(\ldots)}{d\varphi^2} + \left\{\frac{R_1}{R_2}\frac{d}{d\varphi}\left(\frac{R_2}{R_1}\right) + \operatorname{ctg}\varphi\right\}\frac{d(\ldots)}{d\varphi} - \frac{R_1^2}{R_2^2}\operatorname{ctg}^2\varphi(\ldots)\right]. \qquad (3)$$

In our work, we have adopted the following notation: φ is the angle between the normal to the surface and the axis of symmetry, R_1 is the meridian radius of curvature, R_2 is the second principal radius of curvature, $2h$ is the shell thickness, σ is the Poisson ratio, E is the Young modulus, $\lambda^2 = 3(1-\sigma^2)$.

Meissner has shown that the equations (1) and (2) may be transformed into equations of the second order either for shells with a constant curvature meridian, or in all cases when σ is neglected, whose effect, as shown by many authors (2, 3) and confirmed by our investigation, is quite negligible.

Then, instead of the equation (1), we obtain two equations of the following type:

$$L(\Theta) + i\lambda\Theta = 0, \qquad (4)$$

$$L(\Theta) - i\lambda\Theta = 0, \qquad (5)$$

and instead of the equation (2), two similar equations are obtained for U.

Thus, the problem is reduced to the integration of the equation (4), which, as may be seen from the equation (3), will be:

$$\frac{d^2\Theta}{d\varphi^2} + \left\{\frac{R_1}{R_2}\frac{d}{d\varphi}\left(\frac{R_2}{R_1}\right) + \operatorname{ctg}\varphi\right\}\frac{d\Theta}{d\varphi} + \left\{\frac{i\lambda R_1^2}{h\cdot R_2} - \frac{R_1^2}{R_2^2}\operatorname{ctg}^2\varphi\right\}\Theta = 0. \qquad (6)$$

* Θ and U denote all the stresses and displacements of the shells.

Further, we have studied the problem as to for what kind of surfaces the solution of the equation (6) may be obtained in the form of hypergeometrical series.

Investigations * have shown that the equation (6), besides the cases of a sphere, a tore and a cone, analysed by Reissner ([5]) and Meissner ([4]), may be reduced to P. Riemann's type for a katenoidal shell.

For a katenoid:

$$r = a \cdot \operatorname{ch} \frac{z}{a}, \tag{7}$$

the equation (6) will become

$$\frac{d^2\Theta}{d\varphi^2} + \operatorname{ctg} \varphi \cdot \frac{d\Theta}{d\varphi} - \left\{ \frac{i\mu}{\sin^2 \varphi} + \operatorname{ctg}^2 \varphi \right\} \Theta = 0, \tag{8}$$

where

$$\mu = \frac{\lambda \cdot a}{h}.$$

If we introduce the substitution of the variable **

$$\cos \varphi = x, \tag{9}$$

the equation (8) will become:

$$\frac{d^2\Theta}{dx^2} + \frac{2x}{x^2 - 1} \cdot \frac{d\Theta}{dx} - \frac{i\mu + x^2}{(x^2-1)^2} \cdot \Theta = 0. \tag{10}$$

The solution of the equation (10) will be obtained in the following form ($|x| < 1$) ***

$$\left.\begin{aligned} \Theta_1 &= \left(\frac{1+x}{1-x}\right)^{\frac{\sqrt{1+i\mu}}{2}} \cdot F\left(\beta, \beta'; 1 + \sqrt{1+i\mu}; \frac{x+1}{2}\right), \\ \Theta_2 &= \left(\frac{1-x}{1+x}\right)^{\frac{\sqrt{1+i\mu}}{2}} \cdot F\left(\beta, \beta'; 1 - \sqrt{1+i\mu}; \frac{x+1}{2}\right), \end{aligned}\right\} \tag{11}$$

where

$$\beta = \frac{1+\sqrt{5}}{2}, \quad \beta' = \frac{1-\sqrt{5}}{2}.$$

In the same way, the solutions of the equation (5) will be

$$\left.\begin{aligned} \overline{\Theta}_1 &= \left(\frac{1+x}{1-x}\right)^{\frac{\sqrt{1-i\mu}}{2}} \cdot F\left(\beta, \beta'; 1 + \sqrt{1-i\mu}; \frac{x+1}{2}\right), \\ \overline{\Theta}_2 &= \left(\frac{1-x}{1+x}\right)^{\frac{\sqrt{1-i\mu}}{2}} \cdot F\left(\beta, \beta'; 1 - \sqrt{1-i\mu}; \frac{x+1}{2}\right). \end{aligned}\right\} \tag{12}$$

If the complex solutions (11) and (12) be divided into real and imaginary parts, it is easy to obtain four solutions of the formula (1) in the following form:

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* Expressing R_1 by R_2, taking R_2 in the form of $R_2 = a \cos^m \varphi \cdot \sin^n \varphi$ and substituting R_1 and R_2 into the formula (6), we analysed for what values of m and n this equation assumes the form of the equation of the Fuchs type with three singular points.

** By substitutions $\Theta = \sin^{\sqrt{1+i\mu}} \varphi \cdot S$ and $\sin^2 \varphi = \xi$, the equation (8) is reduced to a hypergeometrical one; however, the convergence of series in this case is slow, as is the case of solutions obtained by Meissner for spheres.

*** $x = 1$ and $x = -1$ ($\varphi = 0$ and $\varphi = \pi$) correspond to the infinitely removed points of the katenoid, having no practical interest.

$$I_1 = AP_1 + BQ_1;\ I_2 = BP_1 - AQ_1;\ I_3 = CP_2 + DQ_2;\ I_4 = DP_2 - CQ_2, \quad (13)$$

where, if we introduce the notations:

$$\sqrt{\frac{\sqrt{1+\mu^2}+1}{2}} = a \quad \sqrt{\frac{\sqrt{1+\mu^2}-1}{2}} = b, \quad (14)$$

the values A, B, C, D, P_1, Q_1, P_2, Q_2 entering into the formula (13) will be

$$\left.\begin{aligned} A &= \left(\sqrt{\frac{1+x}{1-x}}\right)^a \cdot \cos\left(b \cdot \ln\sqrt{\frac{1+x}{1-x}}\right), \\ B &= \left(\sqrt{\frac{1+x}{1-x}}\right)^a \cdot \sin\left(b \cdot \ln\sqrt{\frac{1+x}{1-x}}\right), \\ C &= \left(\sqrt{\frac{1-x}{1+x}}\right)^a \cdot \cos\left(b \cdot \ln\sqrt{\frac{1-x}{1+x}}\right), \\ D &= \left(\sqrt{\frac{1-x}{1+x}}\right)^a \cdot \sin\left(b \cdot \ln\sqrt{\frac{1-x}{1+x}}\right); \end{aligned}\right\} \quad (15)$$

$$P_1 = 1 + \frac{\beta\beta'}{1\cdot 2}\cdot\frac{\overline{a+1}}{\overline{a+1}^2+b^2}(x+1) + \frac{\beta(\beta+1)\beta'(\beta+1)}{1\cdot 2\cdot 2^2}\cdot$$
$$\cdot\frac{\overline{a+1}\cdot\overline{a+2}-b^2}{(\overline{a+1}^2+b^2)(\overline{a+2}^2+b^2)}\cdot(x+1)^2 + \frac{\beta(\beta+1)(\beta+2)\beta'(\beta'+1)(\beta'+2)}{1\cdot 2\cdot 3\cdot 2^3}\cdot$$
$$\cdot\frac{\overline{a+1}\cdot\overline{a+2}\cdot\overline{a+3}-b^2(\overline{a+1}+\overline{a+2}+\overline{a+3})}{(\overline{a+1}^2+b^2)(\overline{a+2}^2+b^2)(\overline{a+3}^2+b^2)}\cdot(x+1)^3+\ldots,$$

$$Q_1 = b\left\{\frac{\beta\beta'}{1\cdot 2}\cdot\frac{1}{\overline{a+1}^2+b^2}(x+1) + \frac{\beta(\beta+1)\beta'(\beta'+1)}{1\cdot 2\cdot 2^2}\cdot\right.$$
$$\cdot\frac{\overline{a+1}+\overline{a+2}}{(\overline{a+1}^2+b^2)(\overline{a+2}^2+b^2)}\cdot(x+1)^2 + \frac{\beta(\beta+1)(\beta+2)\beta'(\beta'+1)(\beta'+2)}{1\cdot 2\cdot 3\cdot 2^3}\cdot$$
$$\left.\cdot\frac{\overline{a+2}\cdot\overline{a+3}+\overline{a+3}\cdot\overline{a+1}+\overline{a+1}\cdot\overline{a+2}-b^2}{(\overline{a+1}^2+b^2)\cdot(\overline{a+2}^2+b^2)\cdot(\overline{a+3}^2+b^2)}(x+1)^3+\ldots\right\},$$

$$P_2 = 1 - \frac{\beta\beta'}{1\cdot 2}\cdot\frac{\overline{a-1}}{\overline{a-1}^2+b^2}(x+1) + \frac{\beta(\beta+1)\beta'(\beta'+1)}{1\cdot 2\cdot 2^2}\cdot$$
$$\cdot\frac{\overline{a-1}\cdot\overline{a-2}-b^2}{(\overline{a-1}^2+b^2)(\overline{a-2}^2+b^2)}(x+1)^2 - \frac{\beta(\beta+1)(\beta+2)\beta'(\beta'+1)(\beta'+2)}{1\cdot 2\cdot 3\cdot 2^3}\cdot$$
$$\cdot\frac{\overline{a-1}\cdot\overline{a-2}\cdot\overline{a-3}-b^2(\overline{a-1}+\overline{a-2}+\overline{a-3})}{(\overline{a-1}^2+b^2)\cdot(\overline{a-2}^2+b^2)(\overline{a-3}^2+b^2)}(x+1)^3+\ldots,$$

$$Q_2 = b\left\{-\frac{\beta\beta'}{1\cdot 2}\cdot\frac{1}{\overline{a-1}^2+b^2}(x+1) + \frac{\beta(\beta+1)\beta'(\beta'+1)}{1\cdot 2\cdot 2^2}\cdot\right.$$
$$\cdot\frac{\overline{a-1}+\overline{a-2}}{(\overline{a-1}^2+b^2)\cdot(\overline{a-2}^2+b^2)}(x+1)^2 - \frac{\beta(\beta+1)(\beta+2)\beta'(\beta'+1)(\beta'+2)}{1\cdot 2\cdot 3\cdot 2^3}\cdot$$
$$\left.\cdot\frac{\overline{a-2}\cdot\overline{a-3}+\overline{a-3}\cdot\overline{a-1}+\overline{a-1}\cdot\overline{a-2}-b^2}{(\overline{a-1}^2+b^2)\cdot(\overline{a-2}^2+b^2)(\overline{a-3}^2+b^2)}\cdot(x+1)^3+\ldots\right\}. \quad (16)$$

The convergence of the obtained series is satisfactory (because μ is great), and when P and Q must be calculated with a high degree of accuracy, it is possible to restrict the analysis to three (in the case of P) and two (in the case of Q) members.

Then the solutions of the equations (1) and (2) will be obtained in the following form:

$$\Theta = C_1 I_1 + C_2 I_2 + C_3 I_3 + C_4 I_4, \quad (17)$$

$$U = -\frac{2E}{\lambda}(C_1 I_2 - C_2 I_1 - C_3 I_4 - C_4 I_3), \tag{18}$$

where I_1, I_2, I_3, I_4 are given by the formula (13) and the four arbitrary constants allow to satisfy the boundary conditions.

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ENGINEERING STRUCTURES

THE FACTOR OF SAFETY AS AN INDICATOR OF STRENGTH EQUALITY OF STRUCTURES

By N. STRELECKIJ, Corresponding Member of the Academy

The factor of safety, i. e. the ratio of ultimate load to the working load, is the fundamental coefficient for structural design. The factor of safety is usually considered to be the coefficient of strength equality of structures. If the loads at failure of two structures are different, e. g. because the material of structure I is of a higher strength than that of structure II (for instance, in the latter medium steel is used, and in the former, steel of a higher class), it is usually assumed that, all other conditions being equal, the allowable load of structure I, assuming an equality of strength with structure II, can be increased, as compared with that of structure II, by as much as the load at failure of structure I is greater than that of structure II:

$$\frac{P_{\mathrm{I}}^{all}}{P_{\mathrm{II}}^{all}} = \frac{P_{\mathrm{I}}^{ult}}{P_{\mathrm{II}}^{ult}},$$

or

$$\frac{P_{\mathrm{I}}^{ult}}{P_{\mathrm{I}}^{all}} = \frac{P_{\mathrm{II}}^{ult}}{P_{\mathrm{II}}^{all}} = k,$$

where k is the factor of safety.

This principle is used in designing working loads in all fields of engineering practice in all countries. Analysis shows, however, that the method in question does not agree with conditions existing in reality. This is due to an insufficiently clear understanding of the term «strength equality»

Structures lose their strength and fail owing to a complex of very different causes, all of which are accidental, as, for instance, an accidental inferior quality of material, an accidental defect in the structure, an accidental exceeding of working loads, etc. Structures of normal quality and material cannot fail at a common allowable load, as the stresses developed in such cases are always inferior to the ultimate strength.

Thus, strength depends on chances of failure and equal strength depends on equal chances or, more correctly, on equal probability of failure. Those structures may be called structures of equal strength which have an equal probability of failure.

It is obvious that a failure is possible when the actual forces in a structure will exceed the ultimate possible resistances of the structural material. The latter, being dependent on the defects of the material, are fortuitous and are characterized by a fortuitous value of the ultimate strength (stress) of the material. For steel structures, such a value is the yield point; for concrete structures, the strength of cubes; for cast-iron structures, the ultimate strength, etc. Knowing this stress, we can determine the ultimate load at failure as the product obtained by multiplying the stress by some geometrical factor (area, moment of resistance of the failing structural member) and by a factor depending on the conventionalities of the ultimate strength deter-

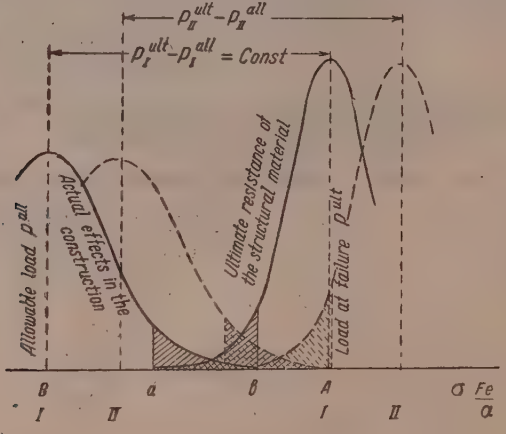

Fig. 1.

mination (for instance, on the conventionalities of the tests of concrete cubes), divided by the influence factor of the breaking load at the place of failure:

$$P^{ult} = \frac{\sigma^{ult} Fc}{\alpha},$$

where F is the geometrical factor, c is the coefficient of transition from the test to working conditions, α is the influence factor. All these values are constant for the given structure (F, α) or may be assumed as such (c).

It is easy to estimate the variability of the value of σ^{ult} from the data of acceptance tests of materials, by plotting a corresponding curve of probability distribution (Hauss, Peerson, etc.)

Actual effects are likewise accidental and may be expressed by a probability distribution curve. The probability of failure depends on the probability of the actual forces being greater than the ultimate strength of material and on the probability of the ultimate strength of material being smaller than the actual influences in the structure. As these probabilities are quite independent, the probability of failure equals their product.

Each of these probabilities equals the area of the corresponding distribution curve within the range of common abscissae, divided by the area of the whole distribution curve (see Fig.). Thus, if the region of common abscissae extends from a to b, the probability that the actual effect will be greater than the ultimate strength is

$$W_1 = \frac{(\Omega_1)_a^b}{\Omega_1},$$

while the probability that the ultimate strengths are smaller than the actual influences is

$$W_2 = \frac{(\Omega_2)_a^b}{\Omega_2}$$

and the probability of failure is $W = W_1 W_2$.

If we take the curves of Gauss and assume that points b and a are such points for which, with the required accuracy, y_b of the first curve and y_a, of the second may be taken as equal to zero,

$$W_1 = \frac{1}{m_1 \sqrt{2\pi}} \int_{b-A}^{a-A} e^{-\frac{x^2}{2m_1^2}} dx,$$

$$W_2 = \frac{1}{m_2 \sqrt{2\pi}} \int_{B-a}^{B-b} e^{-\frac{x^2}{2m_2^2}} dx,$$

where m_1 and m_2 are the standards of the corresponding curves and A and B are the abscissae of the curve centres.

If, owing to changed conditions (for instance, considerations of indeterminability or something else), the load at failure can be increased but all the other characteristics of material qualities remain the same, the centre of the ultimate strength curve will be shifted to the right, while the curve itself will be changed.

As a consequence of an increase of the load at failure, the allowable load may be also increased. If the state of the structure and the working regime do not change, the curve, of actual influences also does not undergo any changes and is only displaced to the right. Having the same equality of failure probability, i. e. strength equality, the areas $(\Omega_1)_a^b$ and $(\Omega_2)_a^b$ must remain unchanged, which results in a shifting of both curves as a whole by the same value. Hence, the load at failure, corresponding to the centre of the ultimate strength curve, and the allowable load, corresponding to the centre of the curve of actual influences, will be displaced by the same value. The state of strength equality is characterized by the constancy of the difference between the allowable load and the load at failure, but not by the constancy of their ratio (factor of safety). This conclusion definitely changes all our possibilities of increasing the allowable loads by increasing the ultimate strength.

The factor of safety is thus by no means a coefficient of strength equality. It relates only to the data of allowable load and load at failure and can not be extrapolated for other data.

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PHYSICS

THE GENERATION OF POWERFUL SOUND VIBRATIONS BY MAGNETOSTRICTION

By E. P. OSTROVSKIJ

(Communicated by S. I. Wawilow, Member of the Academy, 20.I.1937)

The first work on the use of magnetostriction properties in making magnetostriction resonators and oscillators was carried out by Pierce (1). Pierce employed low intensities and was mainly interested in the use of magnet bare stabilizing electrical vibrations. Incidentally, he investigated the velocities of sound in various materials and found that, in the presence of longitudinal vibrations of a bar fixed at the centre, the formula

$$F_0 = -\frac{C}{2l},$$

is satisfied, F_0 being the fundamental frequency of vibration of the bar C—the velocity of sound in it, and l—the length of the bar.

In 1932 appeared an article by Gaines (2), who was the first to point out the possibility of generating powerful magnetostriction vibrations and their transmission into a liquid. He experimented on cold-drawn nickel tubes. The tube used by him was 26 cm in length and gave a frequency of vibrations of 8500 hertz. In using powerful vibrations he succeeded in obtaining a tall jet (up to 6 cm) and also a number of biological effects which had formerly been observed at ultra-sonic frequencies, such as an emulsifying effect, thermal effects, some bactericidal effect, etc. This subject being of paramount interest, we undertook a more detailed study of powerful magnetostriction vibrations and give below some preliminary data relating to the results obtained.

In our first experiments we had used nickel tubes made by the electrolytic process. These electrolytic tubes, having walls of 0.1 mm in thickness, were easily excited, the jets obtained being up to 6 cm in hight. Very good results were obtained with a 24 cm tube, 10 mm in diameter, and with a wall thickness of 0.1—0.2 mm, the frequency obtained being 9000 hertz. Subsequently, we employed nickel tubes made of sheet anode nickel. These heavier tubes made it possible to obtain greater vibrations than with a thin nickel tube made by the electrolytic process. With strong vibrations, we succeeded in obtaining a jet of 8—10 cm with occasional spurts of as much as 20 cm in height.

A disc of the same diameter as the tube was copper-soldered to one end of the tube to serve as radiator. Tin-soldering does not serve the purpose, the disc becoming speedly detached from the tube. Strong vibrations cause the surface of the disc to become dispersed in course of time, the character of the dispersion varying with the kind of metal.

The generating part of the bar excitation apparatus was mounted according to the three-point scheme on a Г- К- 3000 lamp. The voltage of the generating circuit was as high as 4000 V. The circuit consisted of a self-inductance coil, of fixed and adjustable condensers for tuning in with a particular wave length, and of a short multiturn cylindrical coil. The latter set up an alternating magnetic field of such a frequency as was needed for the excitation of the bar.

When used as a vibrator, the tube had its middle point fixed in a rubber stopper, the latter being inserted into the neck of an overturned glass bottle with its bottom cut off (Fig. 1). The upper portion of the tube, together with the disc soldered to its end, was immersed in the liquid that filled the bottle. The lower portion of the tube was inserted into the multiturn coil. During the experiment, the bar became considerably heated, and had to be cooled with a water jet through the lower open end of the tube. The heating of the vibrator is to be avoided, since it reduces the intensity of the vibrations and alters the natural frequency. If the heating is above 360° (the Curie point), the magnetostriction vibrations cease altogether.

While the bar is at work, permanent magnetization must be applied to it. This enables the vibrator to work in the most favourable region of the magnetostriction curve. The measurements made have shown that the most favourable conditions for the bar are those where the magnetostriction coefficient changes most abruptly with the changes of intensity of the magnetic field. In the apparatus used by the writer, additional magnetization was effected by an electromagnet placed at some distance from the bar. Continuous current measurements have shown the optimal magnetizing induction to be $B_0 = 600$ gauss. The heteropolar induction supplied by the multiturn coil with the magnetized bar was $B_{f\max} = 4050$ gauss.

It is to be observed that, when the magnetic field of the magnetizing coil alters f times per second, the nickel bar will undergo periodical alterations of length (shortenings) with a redoubled frequency, i. e. $2f$ times per second [3]. This follows from the fact that the inversion of sign of the field or of the induction, will cause no inversion of sign of the magnetostriction. Therefore the frequency of the vibrator should be equal to half the natural frequency of the bar, i. e. $\frac{F_0}{2}$.

Emulsifying Effect of Magnetostriction Vibrations

Strong magnetostriction vibrations, with frequencies of the order of 10 000 hertz, produce a very considerable emulsifying effect, stable emulsions of transformer oil, benzene and mercury in water being easily obtained. The emulsion is obtained either in the vessel containing the vibrator, or in a separate glass jar, to which the vibrations are imparted through the bottom. In this latter case, the glass jars are sometimes broken by the powerful magnetostriction vibrations, a fact also mentioned by Gaines. We succeeded in obtaining, in the vessel containing the vibrator, over a quarter of a litre of stable emulsion within 1—2 minutes. The emulsions so obtained

were more stable than those produced by piezo-quartz vibrators. Microscopic investigation shows the emulsions obtained to be fairly homogeneous. The transformer oil emulsion was found to have been fully preserved one day after exposure to sound waves. The diameter of the oil patricles was about 1 μ and less. Fig.1 shows a vessel with a nickel vibrator immediately upon completion of emulsifying. The lower milky-white liquid is the emulsion of transformer oil in water. The overlying liquid, lemon-yellow in colour, is the emulsion of water in transformer oil.

Fig. 1

Dispersion of Lead and Other Metals

The vibrations of a magnetostriction vibrator of a frequency of 9405 hertz have the effect of strongly dispersing lead in water. A highly disperse sol of lead of a bluish tint is obtained, lead particles of a larger size being obtained simultaneously. The losses in weight of the lead plate, due to dispersion, if referred to 1 cm^2 of surface, are as follows: a 5-minute exposure in water gave a loss of weight of $137 \cdot 10^{-4} \frac{g}{cm^2}$. The glass jar contained 10 cm^3 of water; the temperature rose during exposure from 21 to 35°. The intensities of the vibrations being equal, dispersion depends not only on the properties of the metal, but also on those of the liquid medium wherein it is dispersed. The same 5-minute exposure applied to a 5% sugar solution in water, gave a loss of $111.7 \cdot 10^{-4} \frac{g}{cm^2}$ for the same volume of water. A 5-minute exposure in vaseline oil (a non-polar liquid) gave a loss of $20.8 \cdot 10^{-4} \frac{g}{cm^2}$.

According to the data obtained at our laboratory by L. R. Solovieva, who used a quartz radiator, at a frequency of 400 000 hertz, the loss in weight of lead due to dispersion was $234 \cdot 10^{-4} \frac{g}{cm^2}$ after an exposure of 40 minutes. Since dispersion is in this range practically proportional to time, a 5-minute exposure would have resulted in a loss of about $29.25 \cdot 10^{-4} \frac{g}{cm^2}$

The loss in weight due to the action of a magnetostriction vibrator is thus seen to be 4.7 times that observable at high frenquencies at equal exposures. There are data available which permit to compare the output of power

in either case. Judging from the thermal effect, the power in the glass jar exposed to the sound waves was, in the case of high frequency vibrations with the quartz plate (frequency 400 000 hertz), 13 watt for a volume of 5 cm³, i. e. 2.6 watt/cm³. In the case of magnetostriction vibrations, the power was 0.27 watt/cm³, i. e. only about one tenth of that put out in the case of a quartz radiator.

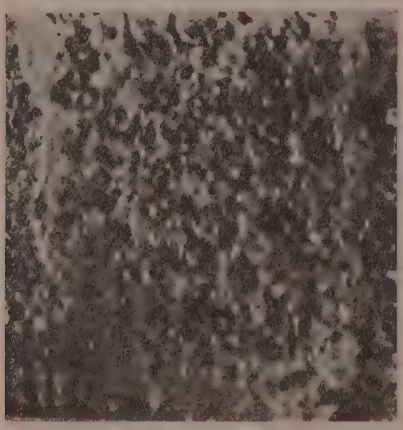

Fig. 2

The surfaces of the lead plates subjected to the action of strong magnetostriction vibrations were found to have been strongly corroded. The plate has been deeply eaten into and looks as it were pitted with pinholes all over its surface. The edges of the holes are raised, lustrous, reminiscent of a freshly fused surface. These holes are not unlike in appearance the surface of lunar craters.

Fig. 2 shows a lead plate after exposure to magnetostriction vibrator.

If alloys of lead and tin containing percentages of either metal varying from 0 to 100% are exposed to sound waves in an aqueous medium under identical conditions, the gradual changes in the nature of the corrosion are easy to observe. The most liable to corrosion is a pure lead surface, or the surface of an alloy of lead with 2% of tin. A further increase in the percentage of tin reduces the corrosion of the surface. Corrosion is at a minimum for alloys containing 50—60% of tin (50—40% of lead), i. e. for those alloys of this series which have the greatest hardness(4)

In addition to alloys of lead and tin, dispersion is also observed with other metals and alloys. We have observed some dispersion in aluminium, copper and nickel, and also in Wood and Lipowitz alloys. The surface of all these metals become corroded, as may be seen with the naked eye.

In conclusion, I wish to express my profound gratitude to S. N. Rževkin, Head of the High Frequencies Laboratory, for his valuable suggestions in connection with the present work. I am also very grateful to L. F. Penkova, of the Karpov-Physico-Chemical Institute, for making the electrolyte nickel tubes.

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BIOPHYSICS

ON THE ACTION OF NON-ADEQUATE STIMULI ON RECEPTORS

By K. CH. KEKČEEV

(Communicated by P. Lasareff, Member of the Academy 21. I. 1937)

The fact that the sensitivity of the receptors of the human organism varies not only under the influence of their adequate stimuli, but also under the influence of stimuli adequate for other receptors, has been demonstrated by the investigations of Urbanchich (1888), P. P. Lasareff (1) (1905 onwards), L. A. Orbeli (2) (1930 onwards) and S. V. Kravkov (3) (1930 onwards), and their collaborators. I have endeavoured to demonstrate the principles of the action of non-adequate stimuli on receptors; also to obtain a change in the sensitivity (E) under the action not only of exteroceptive stimuli (light sound, smell, and so on), as has already been done, but also of stimuli of proprio- and enteroceptive nature.

Both I and my collaborators (Dr. N. M. Zarkh, O. A. Matushenko, A. G. Orliuk) who did most of the experimental work, used the monocular adaptometer of Prof. A. S. Akhmatov, developed in 1934 in our All-Union Institute of Experimental Medicine Laboratory, and a sound frequency generator. We mainly investigated the sensitivity of vision, to a less extent of hearing. About 600 three-hour experiments were done (4).

Acting on the skin surface of the experimental subject with water of various temperatures, we found that a temperature of 19—23° C calls forth an increase in sensitivity of peripheral vision (E), a temperature of 39—40° has no effect, while, finally, the temperature of 45° lowers the value of E (see the table).

Influence of Various Temperatures on E

Subject G. № 56			Subject M., № 56a			Subject G., № 57			Subject M., № 57a			Subject G., № 58			Subject M., № 58a		
$t°$	Before	After	$t°$	Before	After	$t°$	Before	After	$t°$	Before	After	$t°$	Before	After	$t°$	Before	After
20	2.08	5.88	20	2.13	5.88	22	1.96	7.70	23	1.88	7.15	19	1.69	6.67	19	1.69	7.70
42	2.32	2.50	39	2.32	2.32	40	2.04	1.96	40	2.32	2.13	45	1.72	0.94	45	1.72	1.33

Taste stimuli (citric acid, sodium chloride and an infusion of wormwood) caused, when acting for two minutes in small concentrations (1—2%) an increase in E, in higher concentrations (10—20%)—a diminution. The following figures are taken from two experiments.

Subject G., № 118		Subject G., № 119		
		Stimulus	Before	After
Unstimulated	0.50	0.1% wormwood infusion	0.45	2.48(+)
1% citric acid	1.80	0.5% » »	0.52	1.96(+)
5% » »	7.87	4.0% » »	0.52	0.12(—)
10% » »	0.10	5.0% » »	0.45	0.15(—)

During muscular work, the central nervous system is well known to receive an enormous number of afferent proprioceptive impulses. Adrian has shown that this quantity increases considerably with an increase in the intensity of muscular contractions. Using muscular work of small or considerable intensity as a stimulus, we found that work of the first kind causes an increase in E (from 1.37 to 3.33 in subject G., and from 1.56 to 5.23 in subject M.); work of the second kind caused diminution (from 1.85 to 1.22 in subject G., and from 1.59 to 1.09 in subject M.). Summing up, we may say that the following principles seem to be established: small intensities of non-adequate stimuli increase the sensitivity of peripheral vision, medium ones are without effect, large ones decrease sensitivity.

Duration of action has an effect analogous to that of intensity. Thus, for instance, muscular work lasting for 3 minutes increases E, lasting 4 minutes has no effect, lasting 5—6 minutes and more diminishes the value of E.

As stated above, we have also aimed at producing changes in the sensitivity of vision by proprio- and enteroceptive stimuli. The former were obtained by means of muscular contractions as above described, and by passive movements (spinning in a chair, resulting in stimulation of the labyrinthine apparatus). The following record of one experiment (subject G., No 114) may serve as an example:

Time from beginning of adaptation	E
80 min	0.51
105 »	0.51
Spinning for 2 min.	
107 min.	1.96
110 »	1.06
113 »	0.74
131 «	0.51
Spinning for 2 min.	
133 min.	1.80
136 »	0.92
146 »	0.51

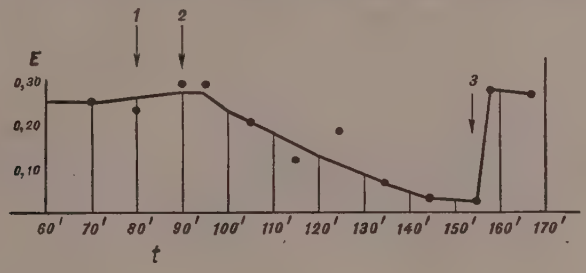
Muscular work or spinning affect the sensory sphere not only through the proprioceptive impulses in which they result, but also by a redistribution of the blood in the body, and by the appearance of various blood constituents (humoral action). Thus we are not dealing here with a «pure» effect of proprioception.

As an enteroceptive stimulus we have made use of the micturition impulse. The subject was at the beginning of the experiment given three glasses of water. The course of the changes in E is shown in the diagram.

We may conclude that the non-adequate stimuli which modify the sensitivity of the cerebral sensory sphere include not only light, sound, smell and taste stimuli (exteroception), but also labyrinthine and muscular (pro-

prioception), and, lastly, enteroceptive stimuli. Thus we are enabled to approach the study of stimuli emanating from the organs of the ventral cavity and the basin, which are usually difficult to study owing to their not being consciously perceived. We are at present developing this question.

Theoretical considerations suggest that the sensitivity of the receptors of the human organism must be influenced also by such stimuli as are not perceived by our sense organs. For instance we have shown (experiments of G. A. Orliuk) that ultra-violet rays (in a dose that caused no visible skin



reaction) lowers the sensitivity of peripheral vision for a period of 60—80 minutes.

If to the above we add the possibility of establishing conditioned connections in the sensory sphere (our publications in the Bull. of Exper. Biol. and Med.), it will be admitted that measurements of the effect of non-adequate stimuli on sight and sound receptors provide a new and probably fertile method for the study of sense organs and of the cerebral sensory sphere.

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CHIMIE

SUR LES MÉTHODES DE DÉTERMINATION DE LA CONSTITUTION DES HYDROCARBURES DE LA SÉRIE C_nH_{2n-2}

Par A. E. FAVORSKIJ, de l'Académie, et M. D. BONE

Jusqu'à présent la chimie organique ne dispose pas d'une méthode commode, permettant la caractéristique de la classe des acétylènes substitués et, en particulier, de la classe des hydrocarbures alléniques.

Plusieurs méthodes ont été proposées, mais toutes ces méthodes ne sont pas libres de tels ou tels défauts.

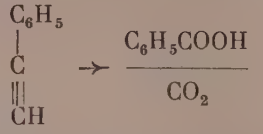
a) La réaction d'addition de l'acide hypochloreux peut servir de base pour caractériser les acétylènes substitués; cependant dans le cas de hydrocarbures alléniques la réaction est bien difficile à effectuer et conduit à la formation des matières dont la séparation n'est pas aisée.

b) Une autre réaction servant à caractériser les hydrocarbures cités consiste en action des acides halogènehydriques. Cependant l'état actuel des travaux sur cette question ne permet pas de faire une conclusion précise sur la structure de ces hydrocarbures. Comme preuve de la structure des composés non saturés, en général, on emploie le plus souvent les méthodes d'oxydation et d'ozonisation. L'oxydation des composés à triple liaison par ces deux méthodes est etudiée suffisamment. Nous avons entrepris des recherches sur l'action de la solution aqueuse de permanganate et d'ozone à 1 p. 100 sur les carbures alléniques. La comparaison de ces deux méthodes dans les deux classes données permet de tirer une série de conslusions sur les méthodes de détermination de la structure des hydrocarbures de la série C_nH_{2n-2}.

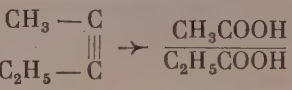
I. Oxydation des hydrocarbures acétyléniques par un permanganate

L'étude de l'oxydation des hydrocarbures acétyléniques par la solution aqueuse de permanganate à 1 p. 100 a déjà été proposée par E. E. Wagner, qui a donné le schème probable de l'oxydation de ces hydrocarbures. D'après son hypothèse les hydrocarbures de la classe d'acétylène et d'allène additionnent deux hydroxyles et une molécule d'eau (ou quatre hydroxyles?) et donnent des hydrates qui se transforment ensuite en anhydrides (1). Dès lors l'étude entreprise par E. E. Wagner a peu avancé. Parmi les travaux plus récents sont à citer les recherhes de G. Bachiérie (2) sur l'oxydation de l'acétylène qui n'ont abouti à rien

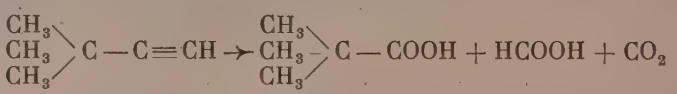
de nouveau. Et, enfin, en ce dernier temps a paru le travail de V. N. Krestinsky et de M. K. Kelbovsky sur l'oxydation des hydrocarbures acétyléniques par le permanganate (3). Conformément à ces recherches, l'acétylène donne à l'oxydation l'acide formique et des traces de l'acide oxalique. Le phénylacétylène fournit par oxydation les acides carbonique et benzoïque:



Le méthyléthylacétylène s'oxyde en acides acétique et propionique:



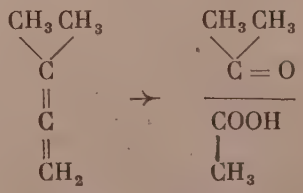
Le butylacétylène tertiaire, en acides triméthylacétique, formique et carbonique:



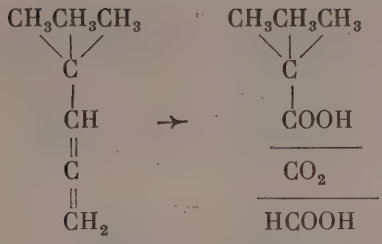
Les auteurs cités n'ayant pu constater dans un seul cas la présence de produits neutres, il est impossible d'établir si l'oxydation de hydrocarbures acéthyléniques se produit d'après le schème des hydrocarbures éthyléniques à l'aide de glycols non saturés avec hydratation consécutive, comme il a été supposé par Wagner, ou bien par une autre voie. Cependant les travaux en question ont établi le fait de dissociation de hydrocarbures acéthyléniques à l'endroit de la triple liaison jusqu'à l'obtention des acides.

II. Oxydation de hydrocarbures alléniques

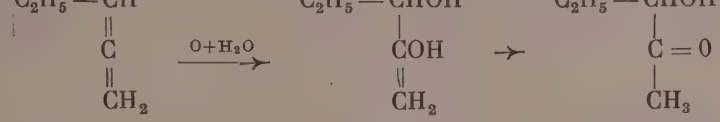
La question de l'oxydation des hydrocarbures alléniques n'a pas été étudiée. Nos expériences ont été précédées par des travaux suivants: en 1887 A. Albicky (4) a oxydé le diméthylallène asymétrique par la solution de mélange de chrome à 10 p. 100 et a obtenu l'acétone et l'acide acétique:



En 1920 O. Alexéjeva (5) ayant oxydé le butylallène tertiaire par la solution de permanganate à 3 p. 100 a obtenu les acides triméthylacétique, carbonique et formique selon l'équation:

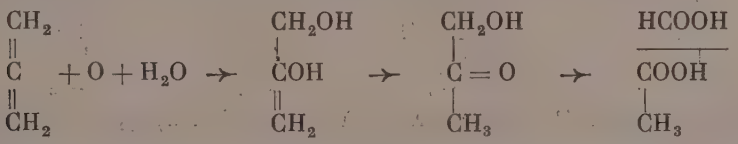


En 1932 Bouis (6) ayant additionné les hydroxyles à l'éthylène à l'aide de la solution aqueuse de chlorate d'argent à 10 p. 100 a obtenu les produits d'addition de deux hydroxyles d'après l'équation:

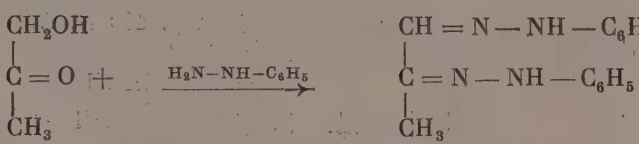


Voilà tout ce qui a été réalisé dans ce domaine avant nos expériences.

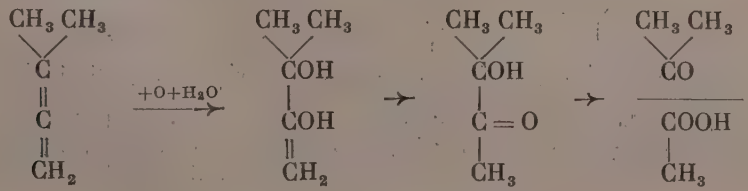
Nous avons étudié l'action de la solution aqueuse de permanganate à 1 p. 100 sur l'allène asymétrique, le triméthylallène. À la suite d'oxydation de l'allène par la solution aqueuse de permanganate à 1 p. 100 on a isolé les acides formique et acétique:



L'oxydation de l'allène par le permanganate de magnésium a donné la possibilité d'isoler un produit neutre—l'acétole en forme de son osazone (température de fusion 154°):

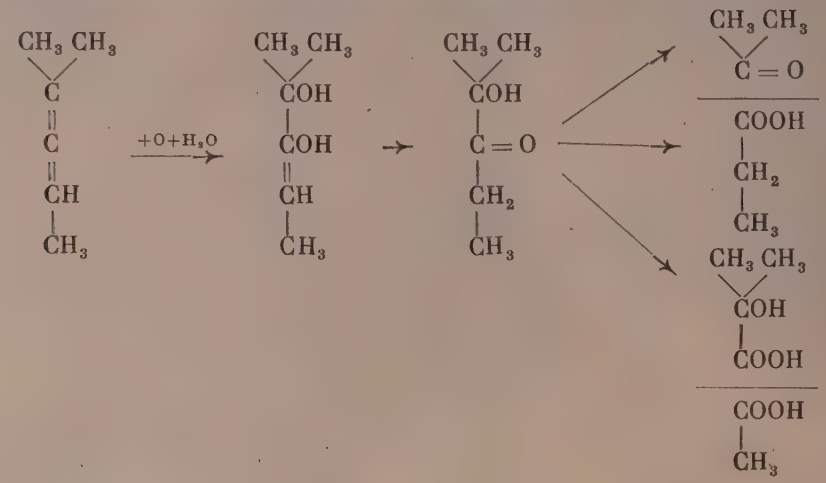


Par oxydation du diméthylallène asymétrique on a obtenu l'acétone et l'acide acétique:

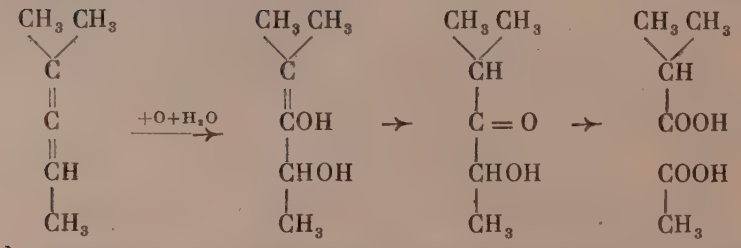


Le triméthylallène a donné par oxydation l'acétone et les acides acétique, propionique, isobutyrique et oxyisobutyrique:

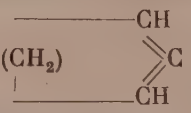
a)



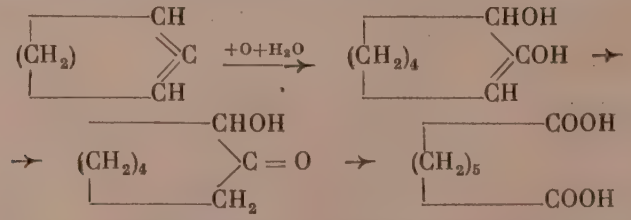
b)



À l'oxydation d'un hydrocarbure à composition C_7H_{10} et à structure



par la solution aqueuse de permanganate à 1 p. 100 N. A. Domnin (7) a obtenu l'acide pimélinique selon l'équation:



En résultat des expériences ci-dessus décrites on peut tenir pour établi que

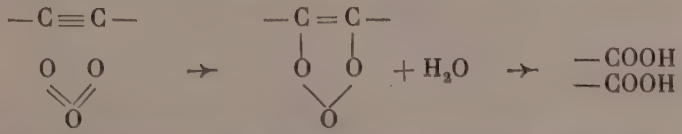
1) Les hydrocarbures alléniques additionnent par oxydation avec la solution de permanganate à 1 p. 100 deux hydroxyles et donnent les glycols non saturés à hydroxyle situé près de la double liaison,

qui ne sont point stables et s'isomérisent immédiatement en cétoalcools correspondants, ces-derniers s'oxydant plus loin, jusqu'aux acides.

2) L'oxydation des hydrocarbures alléniques par la solution aqueuse de permanganate à 1 p. 100 ne peut pas servir de méthode pour prouver la constitution de ces composés, puisque les produits de la réaction ne permettent pas d'établir s'il s'agit d'un hydrocarbure allénique ou bien d'un acéthylène substitué.

Osonization comme méthode de preuve de la constitution des acéthylènes disubstitués et des hydrocarbures alléniques

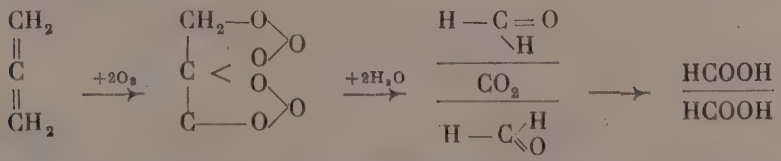
Comme il a été démontré par Harries (8), les composés acétyléniques n'additionnent aisément qu'une seule molécule d'ozone à l'endroit de la triple liaison. La formation d'ozonides et leur décomposition par l'eau se produisent d'après le schème



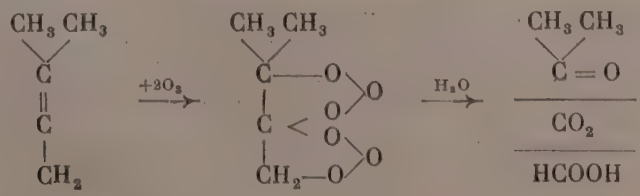
c'est-à-dire la décomposition par l'eau des ozonides obtenus des composés à triple liaison donne exclusivement les acides et la rupture de la molécule a lieu à l'endroit de la triple liaison, de sorte que cette circonstance peut servir comme méthode de preuve de la structure des hydrocarbures acéthyléniques.

Action de l'ozone sur les hydrocarbures alléniques

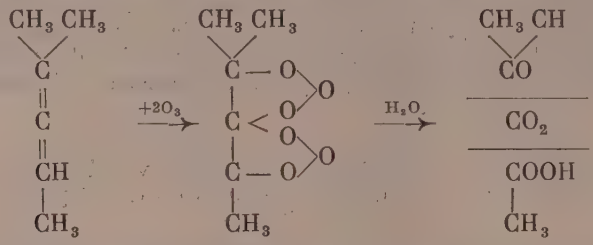
Il n'y a pas de données littéraires sur les hydrocarbures alléniques en ce qui concerne l'action de l'ozone. Nous avons étudié l'action de l'ozone sur l'allène, le diméthylallène et triméthylallène. Par action de l'ozone sur l'allène on a obtenu le formaldéhyde et les acides carbonique et formique:



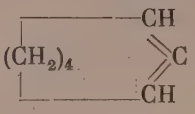
Par action de l'ozone sur le diméthylallène asymétrique sont obtenus l'acétone et les acides carbonique et formique:



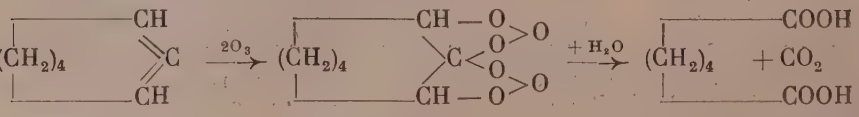
Par action de l'ozone sur le triméthylallène sont obtenus l'acétone et les acides carbonique et acétique:



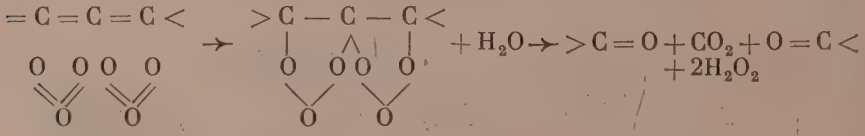
Et, enfin, N. A. Domnin a obtenu par action de l'ozone sur un hydrocarbure à composition C_7H_{10} et à structure



l'acide adipinique:



Les résultats des expériences citées conduisent à la conslusion que les hydrocarbures alléniques additionnent par ozonisation deux molécules d'ozone à chaque double liaison. Les diozonides formés se décomposent par l'eau à l'endroit d'addition de l'ozone, c'est-à-dire à l'endroit de doubles liaisons, et d'après les produits de décompositions l'on peut juger sur la structure de l'hydrocarbure donné. Ce processus de formation des diozonides de hydrocarbures alléniques et leur décomposition par l'eau peut être présenté par les équations:



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1937. Volume XIV, № 8

CHEMIE

ÜBER DIE ZERSETZUNG VON ÄTHERN DURCH EINE LÖSUNG VON METALLISCHEM NATRIUM IN FLÜSSIGEM AMMONIAK

Von P. SCHORIGIN, korrespondierendem Mitglied der Akademie, und S. A. SKOBLINSKAJA

P. Schorigin hatte bereits vor 14 Jahren gefunden (1), dass verschiedene Äther beim Erhitzen mit metallischem Natrium ziemlich energisch nach folgendem Schema gespalten werden:

$$R.O.R' + 2Na \begin{cases} \rightarrow RONa + NaR' \rightarrow R(OH) + R'H \\ \rightarrow RNa + NaOR' \rightarrow RH + R'(OH) \end{cases}$$

Die dazu notwendige Temperatur erwies sich von der Natur der Radikale R und R' abhängig; im Falle von fetten Äthern (R und R' = C_2H_5 oder *iso*-C_5H_{11}) tritt die Zersetzung erst bei 340° ein; die Zersetzung von aromatischen Äthern beginnt schon bei 180° und verläuft exothermisch; noch leichter werden die fettaromatischen Äther, besonders die Benzyläther gespalten (die Zersetzung von Benzylphenyläther beginnt bereits bei seinem Schmelzpunkt, 39°, und vollzieht sich genügend rasch bei 100°).

Wenn die beiden Radikale R und R' voneinander verschieden sind, so kann die Sprengung der Sauerstoffbindungen im allgemeinen nach 2 Richtungen erfolgen, je nach der Bindungsfestigkeit der betreffenden Radikale am O-Atom. Die Versuche von. P. Schorigin mit gemischten Äthern hatten gezeigt, dass verschiedene Radikale bezüglich ihrer relativen Bindungsfestigkeit am O-Atom in folgende Reihe zu ordnen sind (die Bindungsfestigkeit nimmt dabei von links nach rechts zu):

$C_6H_5CH_2-$; C_2H_5-; $C_5H_{11}-$; β-$C_{10}H_7-$; α-$C_{10}H_7-$; C_6H_5-

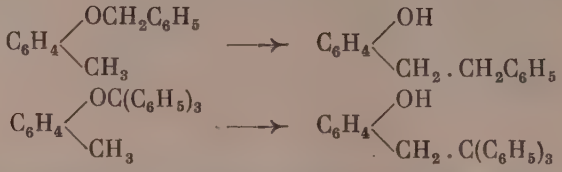
P. Schorigin hatte ausserdem entdeckt (2), dass die Äther von Benzylalkohol, Naphthylkarbinol und Benzhydrol neben einer solchen Spaltung noch eine Umlagerung in die entsprechenden Karbinole (Karbinol-Umlagerung) erleiden:

$$C_6H_5CH_2.O.R \rightarrow C_6H_5.CH(OH).R$$
$$C_{10}H_7CH_2.O.R \rightarrow (C_{10}H_7.CH(OH).R$$
$$(C_6H_5)_2CH.O.R \rightarrow (C_6H_5)_2RC(OH)$$

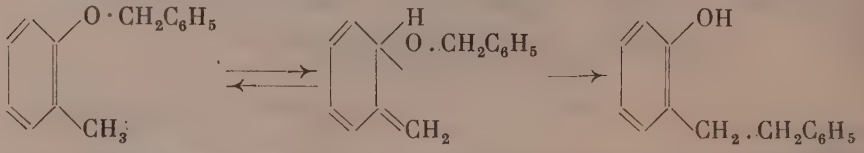
Diese Umlagerung ist wahrscheinlich durch die geringe Bindungsfestigkeit der Radikale $C_6H_5CH_2$, $C_{10}H_7CH_2$ und $(C_6H_5)_2CH$ am ätherischen

O-Atom, sowie durch die Beweglichkeit der an das zentrale C-Atom gebundenen H-Atome bedingt.

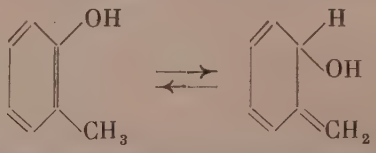
o-Tolylbenzyläther und *o*-Tolyltriphenylmethyläther unterliegen bei der Einwirkung von Natrium einer anderen Umlagerung, bei welcher die Benzyl-, bzw. Triphenylmethylgruppe in die Seitenkette des *o*-Kresols wandert (3):



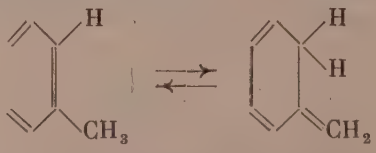
P. Schorigin hatte folgenden Mechanismus dieser Umlagerung (Phenol-Umlagerung) vorgeschlagen:



Die Ursache dieser Phenol-Umlagerung besteht einerseits in der schwachen Bindung der Benzyl-, bzw. Triphenylmethyl-Radikale mit dem O-Atom und andererseits in der Tautomerie des *o*-Kresols und seiner Äther:



Die Tautomerie des *o*-Kresols stellt nur einen speziellen Fall der von P. Schorigin angenommenen Tautomerie von Toluol (4) dar:



In letzter Zeit verwendet man bisweilen die Lösungen von Alkalimetallen in flüssigem Ammoniak: diese Lösungen erwiesen sich in manchen Fällen viel reaktionsfähiger als feste Metalle (Na, K, Li); man ist aber dabei gezwungen, die Reaktionen bei sehr niedriger Temperatur—dem Siedepunkte von NH_3 (—33°)—auszuführen. So hatten z. B. solche Lösungen Kraus(5) beim Studium metallorganischer Verbindungen von Ge, Miller und Siehrs(6), sowie Irving und Muskat (7) für die Darstellung der Alkaliverbindungen der Monosacchariden, Hussey und Scherer(8), sowie Schorigin und Makarowa-Semljanskaja (9) für die quantitative Bestimmung der OH-Gruppen in Zellulose und für die Darstellung der Trinatriumzellulose benutzt. Da wir bei Durchführung letzterwähnter Untersuchung die Methodik der Arbeit mit solchen Lösungen uns angeeignet hatten, so haben wir nun die Versuche über die Zersetzung von Äthern mit Hilfe von Na-Lösungen vorgenom-

men. Dabei haben wir einerseits dieselben Äther, deren Spaltung schon früher von P. Schorigin ausgeführt worden war, andererseits aber die Äther (und Ester) der Zellulose untersucht. (Darüber vgl. die Mitteilung, S. 509.) Die Versuche mit gewöhnlichen Äthern interessierten uns, weil es uns wichtig schien, festzustellen, ob und wieweit diese Äther auch bei — 33° durch Na-Lösung zersetzt werden und ob die obenerwähnten Umlagerungen stattfinden. Man könnte eigentlich von vornherein erwarten, dass reaktionsfähigere fettaromatische Äther (besonders Benzyläther) dabei zersetzt werden, die schwerer zu spaltenden Äther mit fetten Radikalen dagegen intakt bleiben. Die sich dabei bildenden metallorganischen Na-Verbindungen müssten infolge ihrer grosser Reaktionsfähigkeit([10]), mit NH_3 und dem betreffenden Äther sich sogleich umsetzen:

$$RNa + NH_3 = RH + NaNH_2$$
$$RNa + ROR' \rightarrow RONa(\text{bzw. } R'ONa) + R + R'$$

Die Radikale R und R' müssten sich dabei entweder dimerisieren, oder in ein Gemisch von gesättigten und ungesättigten Kohlenwasserstoffen verwandeln. Was nun die Umlagerungen anbetrifft, so wären sie eigentlich nicht zu erwarten, da die Atome und Atomgruppen bei niedriger Temperatur bekanntlich nur wenig beweglich sind, und die Tautomerie bei Toluol und *o*-Kresol erst bei erhöhter Temperatur, bzw. bei energischer Bestrahlung auftritt. Diese, teils auf vorhergehenden Arbeiten von P. Schorigin, teils auf soeben angeführten theoretischen Betrachtungen begründeten Voraussagen wurden in vollem Masse gerechtfertigt. Es erwies sich nämlich, dass *o*-Tolyltriphenylmethyläther, $CH_3C_6H_4O.C(C_6H_5)_3$, durch die Na-Lösung zersetzt wird; bei der Reaktionsdauer von 7 Tagen erhält man *o*-Kresol (die Ausbeute ist ca. 54% der Theorie, bezogen auf kristallinisches *o*-Kresol) und Triphenylmethan; aus den Reaktionsprodukten konnten wir kein Kryptophenol isolieren—es findet offenbar bloss die Zersetzung von Äther und keine Phenol-Umlagerung statt:

$$CH_3C_6H_4.O.C(C_6H_5)_3 + 2Na \rightarrow CH_3C_6H_4ONa + NaC(C_6H_5)_3 \rightarrow$$
$$\rightarrow CH_3C_6H_4OH + HC(C_6H_5)$$

Phenylbenzyläther, $C_6H_5.O.CH_2C_6H_5$, ergab nach 5½-tägiger Einwirkung Phenol (die Ausbeute ist ca. 48% der Theorie) und Dibenzyl; dabei wurde kein Benzhydrol erhalten, die Karbinol-Umlagerung findet also nicht statt. Die Bildung von Dibenzyl kann man durch folgende Reaktionen erklären:

$$C_6H_5.O.CH_2C_6H_5 + 2Na \rightarrow C_6H_5ONa + NaCH_2C_6H_5$$
$$C_6H_5.O.CH_2C_6H_5 + NaCH_2C_6H_5 \rightarrow C_6H_5CH_2.CH_2C_6H_5 + C_6H_5ONa$$
$$2C_6H_5CH_2Na \rightarrow C_6H_5CH_2.CH_2C_6H_5 + 2Na$$

Diphenyläther, $(C_6H_5)_2O$, ergab nach 4½-tägiger Zusammenwirkung mit Na-Lösung Phenol (die Ausbeute beträgt ca. 50% der Theorie); dabei wudre ein Teil von Diphenyläther unverändert zurückgewonnen.

Bei allen diesen Versuchen wurden charakteristische Farbumschläge beobachtet: die Lösung von Natrium in flüssigem NH_3 besitzt bekanntlich tiefblaue Farbe, die während der Reaktion mit Äthern auffallende Änderungen erleidet. Bei Versuchen mit *o*-Tolyltriphenylmethyläther nimmt die Flüssigkeit lebhaft rote Farbe an, die für $(C_6H_5)_3CNa$ charakteristisch ist; im Falle von Phenylbenzyläther schlägt die Farbe nach grüngelb um; bei der Spaltung von Diphenyloxyd bemerkt man die gelbbraune Farbe von

NaC_6H_5 neben der blauen Farbe der Lösung. Alle diese Färbungen verschwinden beim Zusatz von feuchtem Äther nach Verdampfen von NH_3.

Erfolglos erwiesen sich die Versuche, die entsprechenden Karbonsäuren beim Durchleiten von trockenem CO_2-Strom in das Reaktionsgemisch (nach Verdampfen der Hauptmenge von NH_3) zu erhalten; die Ursache dieser Erscheinung ist wahrscheinlich die, dass die metallorganischen Na-Verbindungen schon im Entstehungszustande mit NH_3 und Äther in Wechselwirkung treten, und CO_2 seinerseits mit dem NH_3-Rest Ammoniumkarbaminat bildet.

Negative Resultate wurden mit sorgfältig gereinigtem Diisoamyläther erhalten—es wurde nach 5½-tägiger Einwirkung von Na-Lösung keine Bildung von Isoamylalkohol konstatiert, und die Hauptmenge (ca. $^3/_4$) der verwendeten Äthers wurde in reinem Zustande zurückgewonnen. Die Änderung der Farbe (sie schlägt dabei von tiefblau nach fliederblau um) spricht aber für eine, vielleicht nur geringe Spaltung des Äthers.

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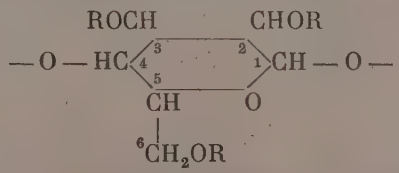
CHEMIE

ÜBER DIE ZERSETZUNG VON ÄTHERN (BZW. ESTERN) DER ZELLULOSE DURCH EINE LÖSUNG VON METALLISCHEM NATRIUM IN FLÜSSIGEM AMMONIAK

Von P. SCHORIGIN, korrespondierendem Mitglied der Akademie, und N. N. MAKAROVA-SEMLJANSKAJA

In der vorhergehenden Mitteilung haben wir über die Zersetzung von verschiedenen Äthern durch die Lösung von metallischem Natrium in flüssigem Ammoniak kurz berichtet. Dieselbe Reaktion haben wir auch mit den Äthern und Estern der Zellulose ausgeführt.

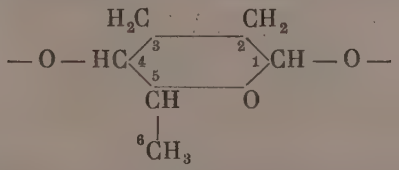
Die Versuche mit Zelluloseäthern (bzw. Estern) müssten sehr interessant vom Standpunkte der Zellulosechemie sein. Die Triäther der Zellulose enthalten bekanntlich in jedem Glukoserest der Hauptvalenzketten die Radikale R, die am 2., 3. und 6. C-Atom stehen:



Ihre Spaltung durch die Na-Lösung könnte nach 2 Richtungen vor sich gehen:

$$\text{Zell}-\text{O}-\text{R} + 2\text{Na} \begin{cases} \rightarrow \text{Zell . ONa} + \text{NaR} \rightarrow \text{Zell . OH} + \text{RH} \\ \rightarrow \text{Zell . Na} + \text{NaOR} \rightarrow \text{Zell . H} + \text{ROH} \end{cases}$$

Es müsste sich also entweder eine Na-Verbindung vom Typus der Alkalizellulose, oder eine bisher noch unbekannte Na-Verbindung der Zellulose und daraus, bei der Zersetzung mit Wasser (oder NH_3), Desoxyzellulose



die von der Zellulose durch Ersatz ihrer Hydroxylgruppen durch H-Atome abgeleitet werden kann, entstehen.

Bei der Einwirkung von CO_2 auf das Reaktionsgemisch könnte man die Bildung von Desoxyzellulosekarbonsäuren, Verbindungen von bisher ebenfalls unbekanntem Typus, erwarten:

$$ZellNa + CO_2 \rightarrow Zell.COONa$$

Man konnte auch nicht voraussagen, ob die glukosidischen Bindungen, welche die einzelnen Glukosereste in Hauptvalenzketten zusammenhalten, sowie die inneren O-Brücken der einzelnen Glukosereste bei der Einwirkung der Na-Lösung intakt bleiben oder gespalten werden.

Wir haben die Versuche mit Zellulose und mit ihren Benzyl- und Methyläthern sowie mit Triazetylzellulose angestellt. Die Versuche mit vollkommen trockenem gebleichtem Linters haben gezeigt, dass die Hauptvalenzketten der Zellulo e dabei keine Spaltung erleiden, denn das nach 2-tägiger Einwirkung von Na-Lösung erhaltene Präparat zeigte keine merkliche Änderungen seiner Eigenschaften (Cu-Zahl des Ausgangslinters 0.03, seine Jodzahl 0.21, nach dem Versuch Cu-Zahl 0.1, Jodzahl 0.29).

Der Benzyläther der Zellulose, welcher $2^3/_4$ Benzylgruppen in jedem Glukoserest enthielt (die Bestimmung von freigebliebenen Hydroxylgruppen wurde nach der Methode von Zerewitinow ausgeführt), wurde durch die Na-Lösung vollständig gespalten (die benutzte Menge des Natriums entsprach 2 Na-Atomen für jede Benzylgruppe), und das Reaktionsgemisch nahm eine rote Farbe, verursacht durch die Bildung von $C_6H_5CH_2Na$, an. Wir haben 5 solche Versuche mit einer Einwirkungsdauer von 6—48 Stdn ausgeführt und dabei Zellulose (ca. 5.5 g aus 8g Äther; JZ 2.0*) und Dibenzyl (ca. 0.5 g) erhalten. Diese Resultate sprechen dafür, dass die Spaltung ausschliesslich im Sinne der Bildung von Alkalizellulose und $C_6H_5CH_2Na$ vor sich geht. Beim Durchleiten von trockenem CO_2-Strom (nach Verdampfen von NH_3) wurde keine Phenylessigsäure—wohl aus obenangeführten Gründen—erhalten; bei einem Versuch konnten wir dagegen eine geringe Menge (ca. 0.17g) von Benzoesäure isolieren; ihre Entstehung kann man nur durch die Spaltung der Benzylgruppe unter Bildung von C_6H_5Na erklären. Bei anderen Versuchen aber wurde die Anwesenheit von Benzoesäure in Reaktionsprodukten nicht konstatiert.

Die Methylzellulose, welche aus Linters nach der Methode von Denham und Woodhouse dargestellt war, enthielt 41.15% (OCH_3) (berechnet für Trimethylzellulose 45.5% (OCH_3); die angewandte Na-Menge entsprach 2Na-Atomen auf jede CH_3-Gruppe und die Zusammenwirkung dauerte 24—48 Stdn. Nach Verdampfen von NH_3 wurde ein Rest von unverbrauchtem Natrium bemerkt; das anhaftende NH_3 wurde durch trockenen N_2-Strom abgetrieben und dann trockener CO_2-Strom durchgeleitet; dabei erfolgte eine heftige Reaktion und die Reaktionsmasse verkohlte sich. Diese unerwünschte Erscheinung konnten wir durch Abkühlen des Reaktionsgemisches beim Durchleiten von CO_2 bis auf 0° und darauffolgende Zersetzung des Reaktionsproduktes durch feuchten Äther (bei Zusatz von Alkohol findet die Verkohlung wieder statt) vermeiden. Der Zelluloserest des Reaktionsproduktes enthielt 24—29% (OCH_3); es wurden also durch die Na-Lösung ca. 35—45% (OCH_3) des Ausgangsäthers abgespalten. Dabei wurde keine Bildung von Essigsäure konstatiert, wohl infolge der Zusammenwirkung von CH_3Na mit NH_3 und Methylzellulose; es gelang dagegen eine kleine Menge (ca. 0.2 g aus 4.2 g Methylzellulose) von zelluloseartiger Substanz mit ausgesprochenem saurem Cha-

* Die Erhöhung der JZ erfolgte offenbar nicht bei der Einwirkung von Na-Lösung sondern bei der Darstellung von Zellulosebenzyläther aus Linters.

rakter zu isolieren. Durch Titration mit 0.1*n* NaOH-Lösung wurde darin die Anwesenheit von 2.6% COOH-Gruppen festgestellt, was der Anwesenheit von 1 Karboxylgruppe in ca. 8 Glukoseresten entspricht. Man kann also schliessen, dass, obwohl die Hauptreaktion im Sinne der Bildung von Alkalizellulose vor sich geht:

$$\text{Zell} \cdot \text{O} \cdot \text{CH}_3 + 2\text{Na} \rightarrow \text{ZellONa} + \text{CH}_3\text{Na},$$

teilweise aber auch die andere Spaltung stattfindet:

$$\text{Zell} \cdot \text{O} \cdot \text{CH}_3 + 2\text{Na} \rightarrow \text{ZellNa} + \text{CH}_3\text{ONa}.$$

Die Bildung metallorganischer Na-Verbindungen der Zellulose äussert sich unter anderem durch sehr heftige Einwirkung von CO_2 und Alkohol auf das Reaktionsprodukt, welche sogar die Verkohlung der Zellulosematerials hervorruft (s. oben).

Wir haben weiter die Benzyl- und Methylzellulose mit Na-Draht in Gegenwart von Benzol in zugeschmolzenen Glasröhren auf kochendem Wasserbade erwärmt. Es erwies sich dabei, dass Methylzellulose beim Erwärmen während 11 Stdn merklich nicht zersetzt wird und beim Öffnen des abgekühlten Rohres kein innerer Druck bemerkt wird; das Reaktionsprodukt enthielt 39.2% (OCH_3). Bei 20-stündigem Erwärmen der Benzylzellulose findet dagegen eine unzweifelhafte Zersetzung statt, denn neben dem Na-Draht erscheint rote Farbe, infolge der Bildung von $C_6H_5CH_2Na$. Die Untersuchung des dabei erhaltenen Zellulosepräparates ist zur Zeit noch nicht abgeschlossen.

Bei Versuchen mit Triazetylzellulose entsprach die angewandte Na-Menge 2Na-Atomen auf jede Azetylgruppe. Die Reaktion dauerte 48 Stdn, das Natirum wurde dabei vollkommen verbraucht. Nach Verdampfen von NH_3 wurde trockener CO_2-Strom durchgeleitet, dabei erwärmte sich das Reaktionsgemisch sehr heftig. Der Gehalt des erhaltenen Produktes an gebundener Essigsäure erwies sich gleich 2.1% (das Ausgangspräparat der Triazetylzellulose enthielt 62.5% gebundener Essigsäure); fast alle Azetylgruppen waren also bei der Einwirkung von Na-Lösung abgespalten und diese Spaltung geht wahrscheinlich nach folgendem Schema vor sich:

$$\text{Zell} \cdot \text{O} \cdot \text{COCH}_3 + 2\text{Na} \rightarrow \text{ZellNa} + \text{CH}_3\text{COONa},$$

obgleich auch eine andere Reaktion (Ammonolysis) nicht ausgeschlossen ist:

$$\text{Zell. O} \cdot \text{COCH}_3 + \text{NH}_3 \rightarrow \text{Zell. OH} + \text{CH}_3\text{CONH}_2.$$

In Reaktionsprodukten wurde die Anwesenheit bedeutender Menge von Essigsäure konstatiert; was nun das Umwandlungsprodukt der Zellulose anbetrifft, so wird es zur Zeit von uns näher untersucht.

Die von uns bei diesen Versuchen angewandte Apparatur ist bereits in einer Abhandlung von P. Schorigin und N. N. Makarova-Semljanskaja beschrieben (1).

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CHEMISTRY

A STUDY OF PERIODICAL PRECIPITATION IN AQUEOUS MEDIA IN CAPILLARIES, FOR THE REACTIONS OF FORMATION OF BARIUM CARBONATE, COPPER CHROMATE AND SILVER SULPHATE

By F. M. ŠEMIAKIN and A. I. LAZAREVA

(Communicated by N. S. Kurnakov, Member of the Academy, 27. I. 1937)

The writers have made a study of the periodical precipitations of barium carbonate, copper chromate and silver sulphate by the Ostwald method (in capillary tubes), with a view to comparing the results thus obtained with those formerly obtained by F. M. Šemiakin, E. A. Fokina and P. F. Mikhalev (1) for the precipitation reactions of barium carbonate and copper chromate, when the investigation was conducted after the Morse method, in a capillary layer between the slide and the glass cover.

In the experiments described below, the writers used solutions the concentration of which was invariably referred to 100 g of solvent (molal* solutions). The substance to be dissolved was taken in quantities corresponding to a saturated solution at 20°C, at the rate of a given number of grams of salt per 100 g of water.

Each salt was recrystallized three times before being used. This procedure was used in preparing solutions of barium chloride, sodium carbonate, potassium chromate, copper sulphate and silver nitrate.

The capillaries were prepared as described in the writers previous communication. The diameter of the capillaries varied in the range of 0.02 to 0.01 cm.

Tables 1 and 2 show the results obtained for the periodical precipitations of barium carbonate. In this reaction, periodical precipitations are obtainable in a rather narrow range of concentrations.

The periodicity constant is seen to increase both with the decrease in the concentration of the outer component, and with the decrease in concentration of the inner component.

Fig. 1

Fig. 2

* The term «molar» occurring in the C. R. Acad. Sci. URSS, vol. IV, No. 8 (1936), p. 370 should be read as «molal».

Table 1

Diameter of capillaries 0.01—0.02 cm $t°_{exp}$=18—20°C

Outer component Na_2CO_3 / Inner component $BaCl_2$	0.8 satur.	0.08 satur.
0.06 satur.	A compact precipitate is deposited. In some capillaries periodical crystallization was observed (20—30 layers)	A compact white precipitate is deposited. It consists of minutest crystals
0.006 satur.	Layers of detached stellate crystals are formed. The interspaces are rather irregular	No precipitate obtained
0.001 satur.	Well-defined layers are obtained after three days. In some cases, in a few hours $\lambda\rho=8\cdot10^{-6}$	—

Table 2

Outer component $BaCl_2$ / Inner component Na_2CO_3	0.6 satur.	0.06 satur.	0.006 satur.
0.08 satur.	Detached stellate crystals divided by more or less regular interspaces (Fig. 1) $\lambda\rho=2\cdot10^{-6}$	Double periodicity: detached crystals and wide layers of very fine precipitate, visible in a reflected light only and reminiscent of chromate of copper layers	Stellate crystals with rather regular interspaces $\lambda\rho=6\cdot10^{-6}$
0.002 satur.	Ill-defined layers. Periodicity constant difficult to determine $\lambda\rho=5\cdot10^{-6}$	Detached stellate crystals irregularly distributed	—

The writers used the same procedure in studying the reaction between potassium chromate and copper sulphate. In this reacton, layers of precipitate can be obtained in a wider range of concentrations than in the previous one.

The results obtained are shown in table 3.

Nor were any layers obtained when the experiment was reversed, i. e., when a 0.01 satur. solution of potassium chromate was used as the outer component, and a 0.008 satur. or a 0.002 satur. solution of copper sulphate was used as the inner component. No layers were obtained also in the case when a 0.006 satur. solution of potassium chromate was used as the outer component, the inner component being a 0.008 satur. solution of copper

Table 3

Outer component, 0.75 satur. solution of copper sulphate
t_{exp}=19°C

Inner component, potassium chromate	Facts observed
0.06 satur.	The precipitate is deposited in well-defined layers consisting of closely packed minute crystals of a brownish orange tinge, divided by interspaces of a yellowish tinge. Layers are formed only just inside the capillary
0.006 satur.	In a passing light the layers are hardly discernible. Detached minute crystals of an irregular shape may be observed. In a reflected or sliding light, well-defined layers may be discerned $\lambda\rho = 1 \cdot 10^{-6}$
0.001 satur.	Layers discernible in a sliding or reflected light only. In a passing light they are invisible $\lambda\rho = 3 \cdot 10^{-6}$ (cf. Fig. 2)
0.0006 satur.	In a reflected light, the layers are easily discernible, it is, however, impossible to determine $\lambda\rho$ since they begin to form at a great distance from the bottom of the capillary
0.0001 satur.	No layers

sulphate. Thus, in the case of this reaction, periodical depositions of a copper chromate precipitate can no longer be obtained if the inner and the outer components of the reactions change places.

Table 4 shows side by side the limiting values of the periodicity constant as obtained by the Morse ([2]) and the Ostwald method respectively. The agreement being a satisfactory one.

Table 4

Periodicity Constant $\times 10^6$

Barium carbonate		Copper chromate	
Morse	Ostwald	Morse	Ostwald
5	6	4	3

Finally, in the reaction between copper sulphate and silver nitrate in capillaries, we have succeeded in obtaining periodical precipitations of silver sulphate monocrystals. The optimal conditions of this reaction are as follows: outer component, 0.75 satur. copper sulphate; inner component, 0.031 satur. silver nitrate. Detached monocrystals of silver sulphate are precipitated and arrange themselves regularly, with strictly defined interspaces.

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CHEMISTRY

COMPARATIVE STUDY OF PERIODICAL PRECIPITATIONS IN AQUEOUS MEDIA BY THE MORSE AND THE OSTWALD METHODS

By F. M. ŠEMIAKIN and A. I. LAZAREVA

(Communicated by N. S. Kurnakov, Member of the Academy, 27. I. 1937)

The writers have studied the influence exercised by the substitution of the inner for the outer component of a reaction on the value of the periodicity constant, and have compared the Morse and the Ostwald methods (in capillaries) from the quantitative point of view. This work is thus a continuation of the study of the influence exerted by these factors on the nature of the periodical depositions of the precipitate (and on the concentration range allowing of periodical deposition), begun in a previous work by F. M. Šemiakin, E. A. Fokina and P. F. Mikhalev (1).

The writers have studied two reactions involving a periodical deposition of the precipitate, viz:

1) $Pb(NO_3)_2 + 2KI \rightleftarrows PbI_2\downarrow + 2KNO_3$,

2) $Na_2CO_3 + HgCl_2 \rightleftarrows HgCO_3\downarrow + 2NaCl$.

The measurements were made with a C. Zeiss comparator microscope after the method described by F. M. Šemiakin, E. A. Fokina and P. F. Mikhalev(2) in the paper mentioned above.

Our experiments have shown both reactions to involve a periodical deposition of the precipitate if the inner and outer components change places.

The results obtained by the Morse method are shown in Table 1.

Higher or lower concentrations of the inner component yield no layers.

The layers are much more difficult to obtain with the carbonate of mercury than with the iodide of lead.

If a saturated solution of nitrate of lead is the outer component, potassium iodide of varying concentrations being the inner component, the layers obtained are much better defined than if the relation between the components of the reaction is reversed.

Experimentation in periodical precipitation in capillaries has not so far been systematic. With a view to a more detailed study of the question we chose the same two reactions. The capillaries method could thus be compared with the Morse method.

Table 1

$t°_{exp.}$ 20—22°C

Outer component	Inner component	Facts observed
$Pb(NO_3)_2$ satur.	KI from 1.0 n to 0.05 n	Well-defined layers. Periodicity constant from $5 \cdot 10^{-6}$ to $14 \cdot 10^{-6}$
KI satur.	$Pb(NO_3)_2$ from 0.05 n to 0.005 n	Well-defined layers, Periodicity constant from $7 \cdot 10^{-6}$ to $9 \cdot 10^{-6}$
$HgCl_2$ satur.	Na_2CO_3 from 1 n to 0.1 n	The layers are not always well-defined. Average periodicity constant $18 \cdot 10^{-6}$
Na_2CO_3 satur.	$HgCl_2$ from 0.25 n to 0.04 n	The formation of layers can just be traced. Average periodicity constant $25 \cdot 10^{-6}$

It has been found expedient to use the following procedure in preparing the capillaries to be used in these experiments.

A tube of high-grade glass is washed, first in a hot chrome mixture, then in distilled water, and finally steamed. Out of this tube capillaries are drawn. It being much more difficult to wash the capillaries after they have been made, this procedure is specially recommended. The capillaries, filled with the solution of the inner component and sealed at one end, were placed, in batches of 25—30 pieces, in test tubes containing the solution of the outer component. The test tubes were then closed up with tightly-fitting stoppers. The diameter of the capillaries varied between 0.01 and 0.003 cm.

The determination of the periodicity constant was made by the method described in a previous work of F. M. Šemiakin, E. A. Fokina and P. F. Mikhalev ([3]).

The number of intervals between the layers is equal to the number of layers n less 1 $(n—1)$.

In the experiments made by the Ostwald method, the inner and the outer component also changed places. The results obtained are given in Table 2.

It is seen from the above experiments that the value of the periodicity constant is considerably affected by the method used in its determination.

In a capillary layer of a wide area (the Morse method), greater values of the periodicity constant are obtained. In a thin capillary column (the Ostwald method), the obtained values of the periodicity constant are lower. The concentration range within which clearly discernible periodical depositions of the precipitate can be obtained is, generally speaking, more narrow in the capillaries method than in the Morse method.

It should also be mentioned that, if the Morse method is used, a periodical precipitation of the carbonate of mercury is much more difficult to obtain than layers of the iodide of lead. Not infrequently, if a series of experiments is repeated in identical conditions, some of them yield layers, while others do not.

Table 2

The Capillaries Method
$t°_{exp.}$=20—22°

Outer component	Inner component	Facts observed
$HgCl_2$ satur.	Na_2CO_3 from 0.5 *n* to 0.2 *n*	In this range of concentrations clearly discernible layers can be obtained. Periodicity constant from $0.7 \cdot 10^{-6}$ to $2.2 \cdot 10^{-6}$
Na_2CO_3 satur.	$HgCl_2$ from 0.25 *n* to 0.025 *n*	In this range, well-defined layers are obtained as detached monocrystals of a yellow or reddish-brown tint. Periodicity constant from $0.6 \cdot 10^{-6}$ to $2.5 \cdot 10^{-6}$
$Pb(NO_3)_2$ satur.	KI 0.5 *n*	Periodicity constant $2.5 \cdot 10^{-6}$
KI satur.	$Pb(NO_3)_2$ from 0.05 *n* to 0.01 *n*	Periodicity constant from $3.4 \cdot 10^{-6}$ to $4.1 \cdot 10^{-6}$ At 0.1 *n* concentrations of $Pb(NO_3)_2$ no layers are discernible. A compact precipitate separates, consisting of coarse irregularly shaped crystals. At 0.001 *n* concentrations, no well-defined layers are obtained

In the course of the reaction of periodical precipitations of mercury carbonate, we had an opportunity of observing the phenomenon of autoformcatalysis in an aqueous medium, analogous to that described by Liesegang (1) for periodical precipitations in gels.

The autoformcatalysis is produced by the bubbles of air, or possibly of carbon dioxide, distributed in the capillary layer, in the path of the propagation of the diffusion field. In this case, the direction of the precipitate layers

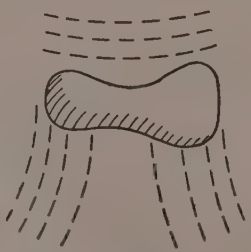

Fig. 1

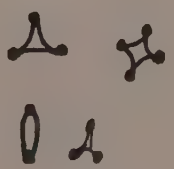

Fig. 2

is altered, and they arrange themselves at right angles to the surface of the bubble (Fig. 1). This phenomenon was observed both on the diffusion of a saturated solution of sodium carbonate into a capillary layer of 0.05 *n* mercury chloride and in the diffusion of a saturated solution of mercury chloride into a capillary layer of 1.0 *n* sodium carbonate.

In the latter case, when diffusion is complete, the evolution of gas bubbles in the apices of individual crystals may be observed at the periphery of the field of diffusion (Fig. 2).

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AGROPHYSIOLOGY

CHARACTERISTICS OF THE GROWTH AND MINERAL NUTRITION OF HEMP WITH SIMULTANEOUSLY MATURING MALE AND FEMALE PLANTS

By L. G. DOBRUNOV

(Communicated by A. A. Richter, Member of the Academy, 17. I. 1937)

While studying the reaction of varieties of hemp to fertilizers, we discovered essential differences between varieties which, to a considerable degree, explain the difference in their yield. We then decided to try to characterize, in this aspect, a new variety of hemp developed by N. N. Griško. The ruling principle in this study was the well-known one that different agricultural technique ought to be applied to the cultivation of different varieties.

On the basis of previous experiments, we assumed a difference between the simultaneously maturing hemp and the mid-Russian variety in the rate of accumulation of dry substance as also in the development of the root system.

Hence, the purpose of the investigation was a study of 1) the accumulation of dry substance and the development of the root system in the various phases of hemp's development; 2) extraction from the soil of the principal nutrient substances and their content in the plants; and 3) sensitiveness to change of concentration of dissolved nutrient substances. During the course of the investigation, we tried to throw light on the principal characters of male and female hemp plants, taking into consideration the heterosexual and diclinous character of the hemp plant.

A study of the growth of roots and above-ground mass was carried out using a soil-sand mixture (in the proportion of 1 to 1). Two series of pots were used in the experiment: 1) pots without fertilizer, and 2) pots with 0.20 g N, 0.15 g P_2O_5 and 0.15 g K_2O per 1 kg of the mixture. Materials experimented on: simultaneously maturing hemp and mid-Russian (Novgorod-Seversk).

The pots were harvested in the following developmental phases of the Novgorod-Seversk hemp: 1) at the beginning of flower-budding, 2) at the beginning of flowering, 3) in full bloom and 4) when the seed was ripe.

There were 12 plants in each pot. Gathering the plants at the periods indicated, the general dry weights of leaves, stalks and seed were determined. The stalks were also analysed for fibre. The total above-ground mass (male and female plants separately) of the last period was analysed for N, P_2O_5 and K_2O.

The root system was thoroughly and carefully washed and, after being dried, was weighed.

To solve the other problems, we employed the method of growing in changed aqueous solutions. This method makes it easy to regulate the concentra-

tion of nutrient substances and to obtain a separate growth of the roots of male and female plants, as was contemplated by the plan of the investigation. The previously tested nutrient mixture of Knop was taken as the basis of this experiment. After preliminary experimentation, the following concentrations of this mixture were decided on: 1.0, 0.1 and 0.01 of normal. The solutions were changed every 2 or 3 days. pH ranged from 5.7 to 5.9.

The conditions under which the experiment was conducted were favourable; the hemp made a good growth. The results are shown below: first from the soil-sand mixture and afterwards from the growth in solutions.

Growth in Soil-Sand Mixture. Measurement of the plants showed that the height of the simultaneously maturing hemp at the period of maturity exceeded the height of the Novgorod-Seversk hemp (for that grown with fertilizer the figures were, respectively, 134.5 and 117.3 cm). The yield of the new variety was considerably greater than that of the Novgorod-Seversk hemp. The additional yield of dry mass, stalks and fibre was 39 to 55% on unfertilized soil and 46 to 69% on fertilized soil. We pass now to an analysis of the reasons for the increased yield of this variety of hemp.

The data on the accumulation of dry substance and weight of stalk on fertilized soil (see Table 1) show the positive side of the simultaneously maturing hemp, which consists in a greater steadiness of accumulation of dry substance throughout the period of vegetation. This may be taken as indicating that the variety in question is less exacting as regards the conditions of growth, since the absence of a short (critical) period of intensive accumulating of dry substance, when the strain and combination of conditions of growth determine the yield, enable the plant in greater degree to utilize favourable conditions throughout the whole period of vegetation.

An analogous steadiness is observed in the increase of weight of the stalks.

Table 1

Accumulation of Dry Substance at Different Phases of Hemp Development (Data for 10 Plants)

Variety of hemp	Date of observation	Dry substance		Stalks	
		Grams	Percentage	Grams	Percentage
Simultaneously maturing	11 VI	3.6	3.4	1.2	1.9
	23 VI	20.2	18.7	8.4	14.2
	17 VII	62.9	58.1	35.2	59.6
	19 VIII	107.8	100.0	58.7	100.0
Novgorod-Seversk	11 VI	4.3	5.9	1.6	3.2
	23 VI	18.8	25.4	8.5	23.0
	17 VII	65.3	88.1	37.2	100.0
	19 VIII	73.7	100.0	35.6	96.2

The somewhat greater duration of the vegetation period of the simultaneously maturing hemp (not only of male, but of female plants, as well) is one of its fundamental biological advantages over the mid-Russian hemp. But this is not all there is to be said about the growth characteristics of the variety and does not explain certain other characteristics of its mineral nutrition. The total absorption of the basic nutrient substances from the soil by the simultaneously maturing hemp exceeds that by the Novgorod-Seversk hemp, as is to be seen from the data of Table 2.

The simultaneously maturing hemp absorbed a great deal more nutrient elements from unfertilized soil, and the difference is still more markedly in favour of the simultaneously maturing variety on fertilized soil. These data

Table 2

Amount of Nutrient Substances Absorbed from the Soil (in Grams, for 10 Plants)

Pot series	Simultaneously maturing hemp			Novgorod-Seversk hemp		
	N	P_2O_5	K_2O	N	P_2O_5	K_2O
With fertilizer	1.87	0.69	2.40	0.77	0.36	1.11
Without fertilizer	0.54	0.35	1.00	0.44	0.20	0.60
In % of unfertilized	346	197	240	175	180	185

show that the simultaneously maturing hemp utilizes the nutrient substances of soil and of fertilizer to a greater extent than does Novgorod-Seversk hemp.

The reason for this phenomenon was sought for in the difference of development of the root systems of the varieties. It was shown in one of our former papers* that the Novgorod-Seversk hemp has a weakly developed root system, especially in the first stages of its growth. This is one of the reasons for its greater need of fertilizer.

Experiments showed that root system of the simultaneously maturing hemp is more strongly developed than in the Novgorod-Seversk hemp. The weight percentage of the roots of Novgorod-Seversk hemp, in the stage of flower-budding, is 8.5%; in the simultaneously maturing hemp it is 10.5%. At the beginning of the flowering stage the percentages are, respectively, 8.8 and 11.9%; in full flowering they are 13.3 and 14.1% respectively. Owing to the prolonged growth period of the male plants in the simultaneously maturing variety, this advantage over the mid-Russian hemp is maintained until the end of the vegetation period.

The data shown above are for male and female plants taken together. It should be noted, however, that the principal characteristics of the new variety are due to the male plants. Maturing at the same time as the female plants, they have not only a longer vegetation period than the male plants of ordinary varieties, but, as experiments have shown, a greater growth, weight and foliation. The fibre content in the stalks of the male plants of the simultaneously maturing variety is almost equal to that of the stalks of the female plants of this variety. However, as regards the yield of fibre from the same number of plants, the superiority is greatly on the side of the simultaneously maturing hemp (41.3% increase on unfertilized soil, and 69.2% on fertilized).

From these facts the difference in dynamics of growth and of accumulation of dry substance in the male plants of the varieties studied becomes plain. While the male plants of the Novgorod-Seversk hemp form the principal mass of the yield during the relatively short period between the beginning of flower-budding and full flowering (i. e. 20 to 25 days), this period of intensive growth is almost twice as long for the male plants of the new variety.

As regards the content of the principal nutrient substances, the male plants of the mid-Russian variety are poorer in nitrogen and phosphoric acid than the female plants. This is explained by the formation of seeds and storing up in them of protein substances and phytin. In the simultaneously maturing hemp, this distinction between the representatives of the sexes is almost entirely absent.

Having a much greater weight, the male plants of the simultaneously maturing hemp absorb more nutrient substances from the soil than do male

* C. R. Acad Sci. URSS, I, 5 (1934).

plants of the Novgorod-Severks hemp. In this respect, the sex representatives of the simultaneously maturing hemp show but little difference. The male plants of the Novgorod-Seversk hemp absorb 2 to 3 times less from the soil than do the female plants.

Growth in Aqueous Solutions. Our further study of the distinctive characters of the growth and mineral nutrition of simultaneously maturing hemp aimed at determining its sensitiveness to decreased concentration of dissolved nutrient substances.

The results of the experiment are shown below.

Table 3

Sensitiveness of Hemp to Change of Concentration of Nutrient Solution (Data in Percentages of Normal Solution taken as 100)

Concentration of Knop's solution	Variety of hemp	Dry Mass	Stalks	Fibre
0.1 normal	Simultaneously maturing	36.0	48.9	50.0
	Novgorod-Seversk	26.2	32.1	29.4
0.01 normal	Simultaneously maturing	20.9	25.2	24.1
	Novgorod-Seversk	18.6	19.3	18.6

The simultaneously maturing hemp showed a smaller decrease of yield than did the Novgorod-Seversk hemp when the concentration of the nutrient substances was decreased. This fact stands out in all the figures on yield. On the basis of our former work* and of these data, we consider it possible to utilize the method of low concentrations for establishing varietal differences with respect to one of the phases of the reaction of variety to fertilizer. Thus, the simultaneously maturing hemp has an advantage over the Novgorod-Seversk hemp in being less sensitive to decrease of concentration of the nutrient solution. This enables it more easily to satisfy its needs as regards absorption of nutrient substances from the soil.

The development of the root systems of the male and female plants of these varieties is also worthy of attention. Below we show the volume and absorbing surface of the roots (as determined by the absorption of methylene blue after Prof. D. A. Sabinin's method).

Table 4

The Development of the Root Systems of Male and Female Hemp Plants (Data for 1 Plant)

Variety of hemp	Volume in cm^3		Absorbing surface in square metres	
	Male	Female	Male	Female
Simultaneously maturing	9.1	9.7	8.5	12.1
Novgorod-Seversk	1.0	14.5	1.1	8.7

The root system of the male plants of the simultaneously maturing hemp is considerably greater than that of the male plants of the mid-Russian hemp. This is one of the principal biological advantages of the new variety, enabling it to satisfy its need for moisture and for nutrient substances more easily.

The data here presented plainly show that a varietal difference in hemps in respect of growth and mineral nutrition is a cause of their difference in productiveness. Probably these data have not, however, revealed all the possible reasons for these differences.

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HYDROBIOLOGY

SOME DATA ON THE VEGETATIVE PRODUCTIVITY OF THE BLACK SEA

By N. V. MOROZOVA-VODJANITSKAJA

(Communicated by S. A. Zernov, Member of the Academy, 26. I. 1937)

A very small number of works dealing with the vegetative productivity of sea has been published so far in USSR, as well as in other countries. Not more than 10 papers may be mentioned containing materials on the quantitative evaluation of marine vegetation.

During the last seven years (from 1929) the author has studied the Black Sea from the viewpoint of its vegetative productivity.

The littoral zone was studied most completely in the course of a year([1,2]). A series of expeditions carried out by the Biological Station in Sevastopol (1933—1936), have allowed to picture the distribution of the biomass of macrophytes at various depths. In shallow water regions, the quantitative evaluation was executed by the method of squares; at depths of over one metre, by means of a bottom sampler; the diving apparatus has been used in some places.

In the Black Sea, the greatest accumulation of algae occurs in the region Sevastopol—Danube—Odessa, at a depths over 30—60 m, where an area of 10 000 km² is covered by the red alga *Phyllophora rubens* Grev ([4]), the quantity of which is over 10 000 000 tons. The part of the sea abundantly covered by *Phyllophora* has been named «The Phyllophora Sea of Zernov» in honour of Academician S. A. Zernov who discovered these beds of *Phyllophora* in 1908.

In the region of the «Phyllophora sea», the *Phyllophora* grows on a bottom of mud and shells; not being attached to the ground, the *Phyllophora* forms beds on cushions of old thalli. The density of *Phyllophora* beds (according to the data of special expeditions of «Khimsoltrust», Odessa) reaches in some places 13 kg per 1 m², the average biomass of algae for the «Phyllophora Sea» being determined at 1.7 kg per 1 m² (raw weight).

Such luxuriant development of algae on muddy grounds at depths of 30—60m has not been discovered in any other region of the Black Sea. The mass development of *Phyllophora* in the north-western part of the Black Sea may be explained by especially favourable physico-chemical conditions of the medium—an abundance of organogeneous elements brought into the sea by four large rivers (Dnieper, Bug, Dniester and Danube), by the presence of a favouring circular current as well as by the specific properties of *Phyllo-*

phora itself, which afford the latter some advantages over all the other species of algae (independence of the ground, capacity to dwell at great depths, vegetative increase and others).

The second place in point of volume of vegetative productivity belongs to the littoral zone of rocks, covered with *Cystoseira barbata*, a brown alga of the family *Fucaceae*.

In the sea regions occupied by the association of *Cystoseira* the biomass of algae reaches in some places 6—7 kg per 1 m², the average biomass for various regions of the sea has been determined at 3 kg per 1 m². All the biomass data show the raw weight of macrophytes.

The beds of the eel-grass *Zostera* situated in places favourable to its development, in sheltered bays with a muddy sand bottom, yield as much as 4 kg of biomass per 1 m², the average for all the districts of the sea so far studied being 1.5 kg per 1 m².

Besides *Phyllophora*, *Cystoseira* and *Zostera* the green algae (*Chaetomorpha chlorotica* up to 6 kg per 1 m², *Enteromorpha*—1.2 kg, *Cladophora*—1.2 kg, *Ulva lactuca*—0.9 kg, *Bryopsis plumosa*—0.5 kg), as well as a few red ones (*Nemalion lubricum* up to 6 kg, *Ceramium rubrum*—0.9 kg, *Gelidium corneum*—0.8 kg, *Polysiphonia subulifera*—0.7 kg, *Laurencia obtusa*—0.6 kg) give a more or less high yield of biomass. All the above figures are maxima. The majority of these species yield scores of grams of biomass per square metre.

The yield of the macrophyte biomass decreases with the increase of the depth at which they grow. Thus, at depths of 0—10 m on littoral rocks the biomass is estimated at several kilograms per square metre; at depths of 10—20 m on shell bottoms, at tens of grams; at depths of 20—30 m (mud with shells), at grams, while deeper still, on muddy grounds (mud with *Mytilus* and *Phaseolina*) the biomass is computed by the tenth and the hundredth part of a gram.

One and the same species of algae gives different quantities of biomass at various depths. For instance, *Cladostephus verticillatus*, *Gelidium crinale*, *Dasya elegans*, *Chondria tenuissima* and some others give a biomass calculated by hundreds of grams when growing on rocks of the littoral zone, while at depths of 15—20 m on a shell ground just the same species form considerably smaller thalli and more sparse beds which hardly give 10—20 grams per 1 m².

The volume of the algal biomass also depends upon the physical nature of the bottom and the position and dip of the surface which is clothed by algae. Vulcanic substrata are covered by the vegetation in a much less degree, than sedimentary ones. The vulcanic strata in the vicinity of Karadagh (north-eastern part of the Crimean peninsula) produce 500 g per 1 m², while sedimentary rocks give as much as 1 800 g under identical ecological conditions. This may be accounted for by the physical properties of the substratum (²).

There is no difference either in the systematical composition or in the biomass between the algae covering concrete constructions and those vegetating on a natural rocky bottom if the other ecological factors are identical.

A sloping surface is a more favourable factor than a vertical one. On a substratum having a sloping surface the vegetative overgrowth gives a biomass 5—6 times greater than it does in a vertical position, which may be due to different conditions of illumination and to a different exposure to the impact of the waves.

The production or the increase of the macrophyte biomass in the Black Sea was determined only for the vegetation of the shallow littoral zone, down to a depth of 1 m. The maximum yearly production, 10—17 kg per 1 m² of the

bottom, is observed in sheltered regions of the sea in bays and lagoons; in the open sea the production has been determined at 7.8 kg per 1 m².

Of all the various species of algae, *Cystoseira barbata* and *Chaetomorpha chlorotica* yield the largest yearly increase of biomass (6 kg per 1 m² raw weight); the yearly increase of substance is for the majority of species less than 500 g per 1 m².

The rate of increase of the biomass changes during the year. The highest rate of growth is noted for *Chlorophyceae* and some of *Rhodophyceae* during the spring time. Under favourable conditions of the season and habitat *Bryopsis*, *Ulva*, *Cladophora* and *Enteromorpha* form one day 30—50 g of new substance per 1 kg of the total weight of the algae (raw weight). *Ceramium rubrum* (40 g per 1 kg), *Ceramium diaphanum* (32 g per 1 kg) and *Laurencia obtusa* (33 g per 1 kg) have a higher rate of growth than any other red algae.

On the basis of the quantitative evaluation of bottom vegetation the writer has endeavoured to make out a scheme of the distribution of the vegetative productivity among the principal regions (near the Caucasian shores, near the Crimean shores and in the north-western part of the Black sea).

The computations were made on the basis of the following data which are generalized for all the regions (except the Phyllophora Sea).

Biomass of macrophytes	at a depth of 0—10 m on littoral rocks	1000 g
	» » » » 10—20 » sand with shells	20 »
	» » » » 20—30 » mud » »	5 »
	» » » » 30—50 » »	1 »
	» » » » 50—90 » »	0.1 »

The vegetative productivity was determined from the total biomass of macrophytes yielded by 1 m of coastal line from the shore to the maximum depth of the habitat of algae (90—100 m according to N. N. Voronikhin).

The breadth of the algal zone is not the same in various parts of the sea and depends upon the steepness of the dip of the sea bottom near the coasts. The writer considers the breadth of the algal zone near the Caucasian coasts to be about 3 km; near the Crimean coasts, about 7 km, reaching 150 km in the north-western part of the Black sea.

The volume of the total biomass of macrophytes in the algal zone may be estimated at the following figures per metre of coastal line at depths of 0—100 m.

Near the coasts of the Crimea—130 kg raw weight
» » » » » Caucasus—256 kg » »
In the north-western part of the Black sea—135 tons raw weight.

The maximal biomass (135 tons) observed in the north-western part of the Black sea is due to the presence of Phyllophora beds in the region of the «Phyllophora Sea». Near the coasts of the Crimea the vegetative productivity is only half (130 kg) that of the coasts of the Caucasus (256 kg). This may be due to a steeper incline of the bottom of the coasts of the Crimea as well as by a narrower coastal zone of rocky ground covered by particularly abundant vegetation.

In the north-western part of the Black sea the region situated at a depth of 30—60 m shows the greatest productivity; the *Phyllophora* beds lying at a depth of 30—60 m give 98 per cent (130 tons) of the 135 tons of the total biomass yielded by 1 m of coastal line.

Near the Crimean and the Caucasian coasts the region of coastal rocks lying at a depth of 0—10 m gives 96—97 per cent of the whole biomass of ma-

crophytes, while the other regions, situated at depths ranging from 10 to 100 m and extending over many kilometres from the shore possess along their whole extent a biomass of 5—7 kg, or 3—4 per cent of the total biomass yielded by 1 m coastal line.

The data contained in this paper are only approximate, showing as they do the order of magnitudes only, and may be used principally in a comparative analysis of vegetative productivity of the Black sea in its various parts.

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ERRATA

In the M. I. Saltykovskij's paper (1937, vol. XIV, № 4), in the right part of the table 1, the title «Winter wheats yarovized» is to be replaced by «Winter wheats non-yarovized».

In the L. S. Berg's paper (1936, vol. IV, № 7, p. 345) for *Acanthopterygian* read *Actinopterygian*.